ORIGINAL ARTICLE

Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell

Orawan Sirichote[1], Wanna Innajitara[2], Laemthong Chuenchom[3], Doungporn Chunchit[3] and Kanokrat Naweekan[3]

Abstract

Sirichote, O.[1], Innajitara, W.[2], Chuenchom, L.[3], Chunchit, D.[3] and Naweekan, K.[3]
Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell
Songklanakarin J. Sci. Technol., 2002, 24(2) : 235-242

The adsorptions of iron (III) from aqueous solution at room temperature on activated carbons obtaining from bagasse, pericarp of rubber fruit and coconut shell have been studied by atomic absorption spectrophotometry. The activated carbons were prepared by carbonization of these raw materials and followed by activation with $ZnCl_2$. The adsorption behavior of iron (III) on these activated carbons could be interpreted by Langmuir adsorption isotherm as monolayer coverage. The maximum amounts of iron (III) adsorbed per gram of these activated carbons were 0.66 mmol/g, 0.41 mmol/g and 0.18 mmol/g, respectively. Study of the temperature dependence on these adsorptions has revealed them to be exothermic processes with the heats of adsorption of about -8.9 kJ/mol , -9.7 kJ/mol and -5.7 kJ/mol for bagasse, pericarp of rubber fruit and coconut shell, respectively.

Key words: activated carbons, bagasse, pericarp of rubber fruit, coconut shell, Langmuir adsorption isotherm

---

[1]Ph.D. (Physical Chemistry), Asst. Prof., [2]B.Sc. (Chemistry), Asst. Prof., [3]B.Sc. (Chemistry), Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112 Thailand.
Corresponding e-mail : sorawan@ratree.psu.ac.th
Received, 13 September 2001 Accepted, 2 March 2002

บทคัดย่อ

อรวรรณ ศิริโชติ วรรณา อินนาจิตร แหลมทอง ชื่นชม ดวงพร ชวนชิต และ กนกรัตน์ นาวีการ
การดูดซับไอออนเหล็กบนถ่านกัมมันต์ที่เตรียมจากชานอ้อย เปลือกลูกยาง และกะลามะพร้าว
ว. สงขลานครินทร์ วทท. 2545 24(2) : 235-242

การศึกษาการดูดซับไอออนเหล็ก (Fe^{3+}) ในสารละลายน้ำบนถ่านกัมมันต์ที่อุณหภูมิห้อง ทำโดยใช้วิธีอะตอมมิกแอบซอร์พชันสเปกโทรสโกปี การเตรียมถ่านกัมมันต์จากชานอ้อย เปลือกลูกยาง และกะลามะพร้าว ด้วยวิธีคาร์โบไนเซชันแล้วกระตุ้นด้วย $ZnCl_2$ การดูดซับไอออนเหล็ก บนถ่านกัมมันต์เหล่านี้ มีพฤติกรรมแบบแลงเมียร์ไอโซเทอร์ม ซึ่งอธิบายว่าไอออนเหล็กปกคลุมจนเต็มพื้นที่ผิวของถ่านกัมมันต์แบบชั้นเดียว ปริมาณไอออนเหล็กที่ถูกดูดซับสูงสุดบนถ่านกัมมันต์เหล่านี้ มีค่าเท่ากับ 0.66 mmol/g, 0.41 mmol/g และ 0.18 mmol/g สำหรับถ่านกัมมันต์จากชานอ้อย เปลือกลูกยาง และกะลามะพร้าว ตามลำดับ จากการศึกษาการดูดซับที่ขึ้นกับอุณหภูมิ พบว่า เป็นกระบวนการคายความร้อนที่มีค่าความร้อนของการดูดซับ เท่ากับ -8.9 kJ/mol , -9.7 kJ/mol และ -5.7 kJ/mol สำหรับถ่านกัมมันต์จากชานอ้อย เปลือกลูกยางและกะลามะพร้าว ตามลำดับ

ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112

Activated carbon has been reported to have high and fast adsorption capacities (Chaiwattananont *et al*., 1998) due to its well-developed porous structure and tremendous surface area (Manahan, 1991). The important application of activated carbon is for water purification. The groundwater in urban and rural areas of the lower part of southern Thailand contains appreciable levels of dissolved calcium, magnesium, iron and manganese. These substances contribute to hardness and total solids in water. Activated carbon can play an important role in improvement of water qualities for drinking and domestic uses.

In this study we were interested to prepare powdered activated carbons from abundant local agricultural by-products such as bagasse, pericarp of rubber fruit and coconut shell. The samples were prepared by carbonization and followed by chemical activation at various activation parameters (Hassler, 1974; Ferro-Garcia *et al*., 1988). In the carbonization step the carbon was produced by charring the raw material in the absence of air below 600 °C. The char was then activated by some specific chemical in order to develop porosity, increase the surface area and leave the carbon atoms in arrangements with high affinities for adsorption. After obtaining these activated carbons, some characteristics such as the iodine number, the methylene blue number and the BET surface area were analysed. The adsorption behavior of iron ion in aqueous solution on each of these three activated carbons was then investigated. Activated carbon has a reduction ability due to the organic functional groups such as phenolic, lactone, carbonyl, and quinone. Ferric ion, therefore can be readily reduced to ferrous ion by these surface organics (Huang and Blankenship, 1984; Uchida *et al*., 2000). However, there has been no reports on the reduction and adsorption mechanisms of iron ion on activated carbon. In this work the total adsorptions of iron ion from aqueous solution on these three activated carbons were evaluated by atomic absorption spectrophotometry.

Materials and Methods

Preparation of activated carbons

The production process of activated carbons from bagasse, pericarp of rubber fruit and coconut shell, all consisted of carbonization and chemical activation with $ZnCl_2$. Each dried raw material was cut into small pieces approximately 1 cm^2 and placed into stainless steel box with cover. The carbonization was then conducted in a muffle furnace at 300 °C, 400 °C and 450 °C for bagasse, pericarp of rubber fruit and coconut shell, respectively. The heating period was 3 hrs for all materials.

After carbonization, the residual char was ground using a laboratory jar mill to pass through a 325 mesh (40-45 µm) sieve. The chemical activation was done in the next step by mixing the ground char with concentrated solution of $ZnCl_2$ in the crucible. Activation had been carried out by varying sample to $ZnCl_2$ ratio and activation temperature. Sample to $ZnCl_2$ ratios were 1:2 and 1:3 by weight. The samples were activated at 600 °C and 800 °C for 3 hrs in a muffle furnace. The obtained activated carbon was washed with 5% HCl solution followed by hot water to remove chloride including zinc compounds and dried at 110 °C for 3 hrs. The obtained activated carbons were kept in a dessicator and were characterized for iodine number, methylene blue number (in accordance with American Standard of Testing Material, 1999) and BET surface area. The iodine number gives an indication of the adsorption capacity of activated carbon in micropores. While the methylene blue number gives an indication of the adsorption of activated carbon for molecules having similar dimensions to methylene blue and the existence of mesopores on surface area of activated carbon (Vitidsant *et al*., 1999).

Adsorption experiments

All activated carbons shown in Table 1 were used to study adsorption of iron ion. Adsorption equilibrium study of iron ion was carried out in a 250 mL stoppered conical flask by adding 0.2500 g of activated carbon to 20 mL of $FeCl_3$ solution. The concentrations of iron (III) in the $FeCl_3$ solution were varied in the range of 50 to 800 ppm. All experiments were done at room temperature. After gentle shaking for 1 hr in a mechanical shaker, the contents were filtered through filter paper No.1 by neglecting the first 5 mL of the filtrate in order to saturate the filter paper with $FeCl_3$ solution. Concentrations of iron ion in the

Table 1. Some characteristics of three types of activated carbons at different activation temperatures and sample to $ZnCl_2$ ratios.

Raw material	Activation temperature (°C)	Sample to $ZnCl_2$ ratio	IA (mg/g)	MB (mg/g)	S_{BET} (m^2/g)
Bagasse	600	1:2	934	281	1150
		1:3	935	280	1239
	800	1:2	1212	283	1396
		1:3	1192	279	1553
Pericarp of rubber fruit	600	1:2	1063	276	1508
		1:3	1027	280	1549
	800	1:2	1260	281	1472
		1:3	1281	281	1737
Coconut shell	600	1:2	1055	164	1097
		1:3	1281	164	1140
	800	1:2	1002	162	970
		1:3	907	164	899

IA = iodine number, MB = methylene blue number, and S_{BET} = BET surface area
The BET surface areas were analysed by Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University.

filtrate were then determined by Perkin-Elmer AAnalyst 300 model atomic absorption spectrophotometer. The amount of iron ion adsorbed was calculated based on the difference between the iron ion concentration in aqueous solution before and after adsorption.

For adsorption at higher temperatures iron solutions and activated carbons in the stoppered conical flasks were shaken in a thermostat shaker bath maintained at 32 °C, 42 °C, 51 °C, and 70 °C for 1 hr. Only one concentration of iron ion solution that exhibited maximum adsorption on each type of activated carbon was used to run these experiments.

Results and Discussion

Table 1 shows some characteristics of three activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell. When comparing each raw material at different activation conditions, it is found that bagasse and pericarp of rubber fruit activated at 800 °C with sample to $ZnCl_2$ ratio of 1:3 and coconut shell activated at 600 °C with sample to $ZnCl_2$ ratio of 1:3 give the greatest values of iodine number (IA) of 1200. Their BET surface areas also give the same trend as their iodine numbers. The methylene blue numbers (MB) of activated carbons obtained from bagasse and pericarp of rubber fruit activated at various conditions are the same. Their values of 280 are greater than those for activated carbons obtained from coconut shell with values of 160.

The experimental equilibrium isotherms at room temperature and different feed concentrations of iron (III), $C_{initial}$ are shown in Figure 1. In this figure all types of activated carbons were prepared by activation with a sample to $ZnCl_2$ ratio of 1:3 at 600 °C. On each isotherm the amount adsorbed increased with feed concentration and became level off at higher feed concentrations. The maximum adsorption capacities were read when they became independent of the feed concentrations. The amount of iron ion adsorbed on all types of activated carbons increased in the increasing order from coconut shell to pericarp of rubber fruit and highest for bagasse.

The Langmuir equation is expressed as follows (Wan Ngah and Liang, 1999):

$$\frac{C}{X} = \frac{C}{X_{max}} + \frac{1}{X_{max} b} \qquad (1)$$

where C is the equilibrium or final concentration of iron ion in mmol/L, X is the amount of iron ion adsorbed per unit weight of activated carbon at equilibrium concentration (mmol/g), X_{max} is the maximum adsorption at monolayer coverage

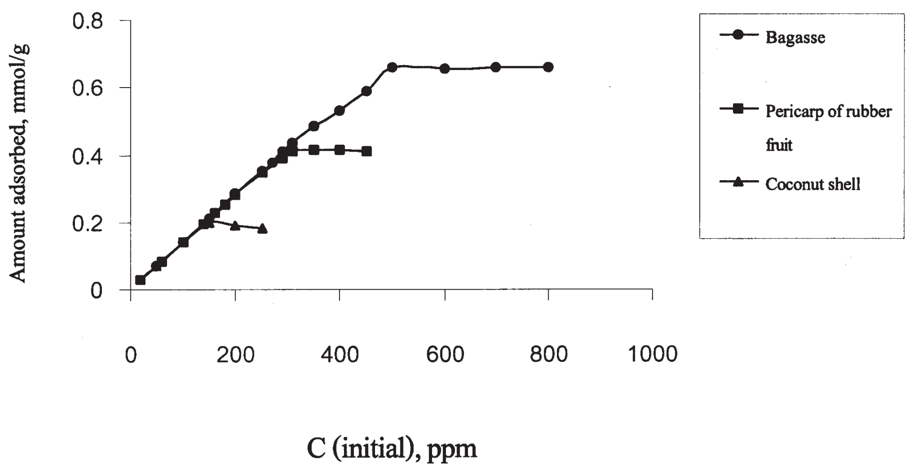

Figure 1. Adsorption isotherms of iron ion on three types of activated carbons at room temperature.

(mmol/g), and b is the adsorption equilibrium constant (L/mmol).

From equation (1) the plot of C/X versus C should give a straight line of slope $1/X_{max}$ and an intercept of $1/X_{max}b$ on the C/X axis. This linear plot shows that the adsorption obeys the Langmuir isotherm model. The Langmuir adsorption isotherm is based on the characteristic assumption that only monolayer adsorption takes place (Shaw, 1980).

Figures 2 to 4 show the Langmuir plots that have the greatest values of iron adsorption on

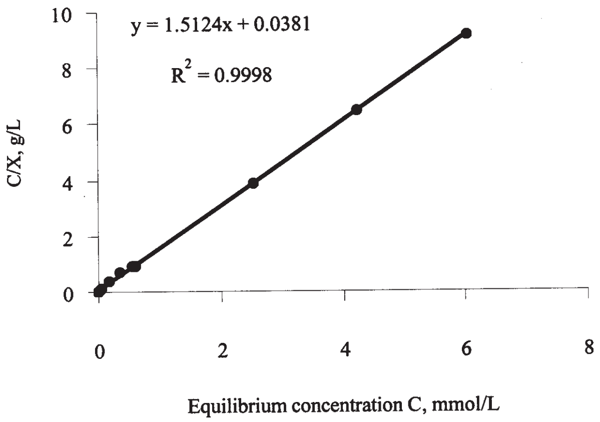

Figure 2. Langmuir plot for the adsorption of iron ion on activated carbon obtained from bagasse.

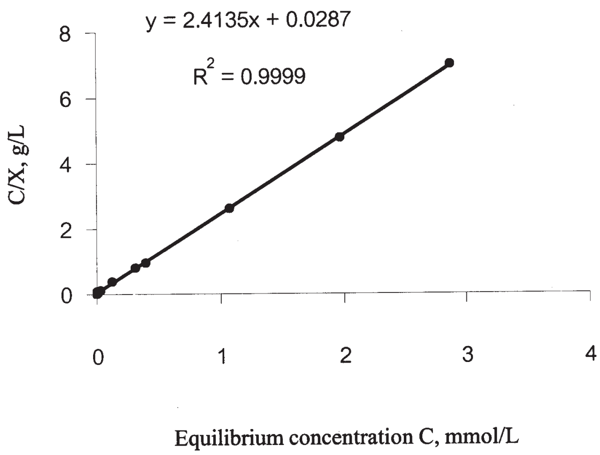

Figure 3. Langmuir plot for the adsorption of iron ion on activated carbon obtained from pericarp of rubber fruit.

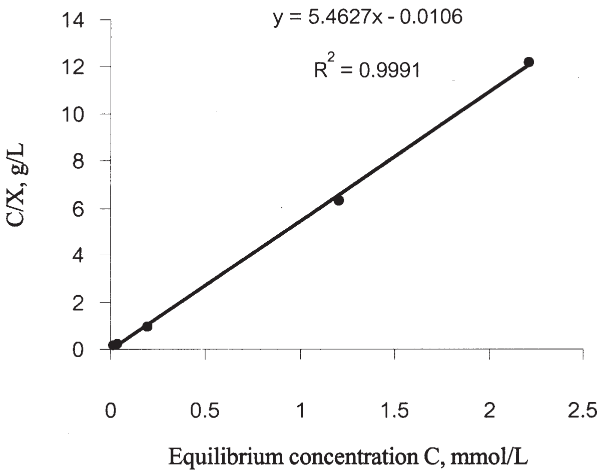

Figure 4. Langmuir plot for the adsorption of iron ion on activated carbon obtained from coconut shell.

three types of activated carbons with a sample to $ZnCl_2$ ratio, 1:3 and activation temperature at 600 °C. The values of X_{max} calculated from slopes of the Langmuir plots for all activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell at room temperature are in the range 0.25 - 0.66 mmol/g, 0.11 - 0.41 mmol/g and 0.12 - 0.19 mmol/g, respectively.

The temperature dependence of the adsorption of iron ion on these activated carbons is shown in Figure 5. The experimental result shows that the amount of iron ion adsorbed on activated carbons decreased with increasing adsorption temperature. This suggested that the adsorption mechanism was physical adsorption, in contrast to chemical adsorption in which the amount of adsorbate adsorbed on an adsorbent increases with increasing adsorption temperature (Uchida *et al.*, 2000).

The heat of adsorption was calculated by applying the Clausius- Clapeyron equation to the adsorption isotherm as follows (Alberty and Silbey, 1992; Tanada *et al.*, 2000):

$$\frac{dP}{dT} = \frac{P\Delta H_{vap}}{RT^2} \qquad (2)$$

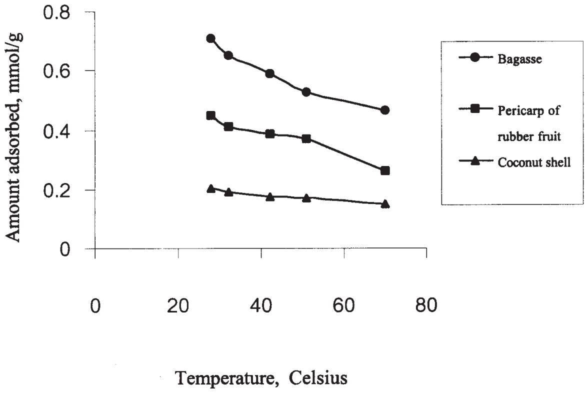

Figure 5. Plot of the amount of adsorbed iron ion on three types of activated carbons versus temperature in Celsius.

where P is the equilibrium pressure of gas, T is the absolute temperature, ΔH_{vap} is the heat of vaporization, and R is the gas constant. On rearrangement equation (2) becomes

$$\frac{dP}{P} = \frac{\Delta H_{vap}}{RT^2} dT \quad (3)$$

$$d \ln \frac{P}{P^o} = \frac{\Delta H_{vap}}{RT^2} dT \quad (4)$$

where P^o is the standard pressure used.

Replacement of P by CRT and P^o by C^oRT from ideal gas law where C is the molar concentration and C^o is the standard value of the molar concentration (1 mol/L) equation (4) becomes

$$d \ln \frac{C}{C^o} = \frac{\Delta H_{vap}}{RT^2} dT \quad (5)$$

For adsorption in solution the ΔH_{vap} is replaced by ΔH_{ads} which is the heat of adsorption.

Integrating on the assumption that the ΔH_{ads} is independent of temperature and concentration and since the term $\ln C^o$ is equal to zero, equation (5) yields

$$\int d \ln C = \frac{\Delta H_{ads}}{R} \int T^{-2} dT \quad (6)$$

$$\ln C = -\frac{\Delta H_{ads}}{R} \frac{1}{T} + c \quad (7)$$

where C is the molar concentration of adsorbate and c is the integration constant. Plot of ln C versus 1/T should give a straight line of slope $-\Delta H_{ads}/R$.

The plots of applied Clausius-Clapeyron equation to adsorption isotherm in equation (7) as ln C versus 1/T are shown in Figures 6 to 8.

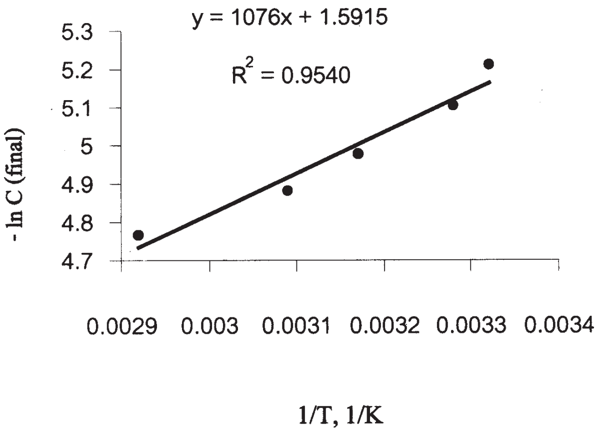

Figure 6. Clausius-Clapeyron plot at various temperatures for adsorption of iron ion on activated carbon obtained from bagasse.

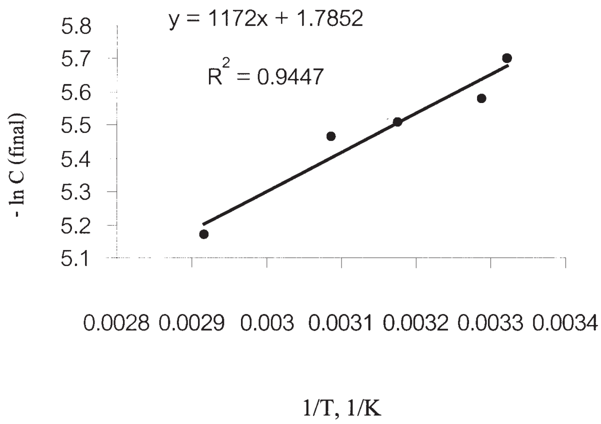

Figure 7. Clausius-Clapeyron plot at various temperatures for adsorption of iron ion on activated carbon obtained from pericarp of rubber fruit.

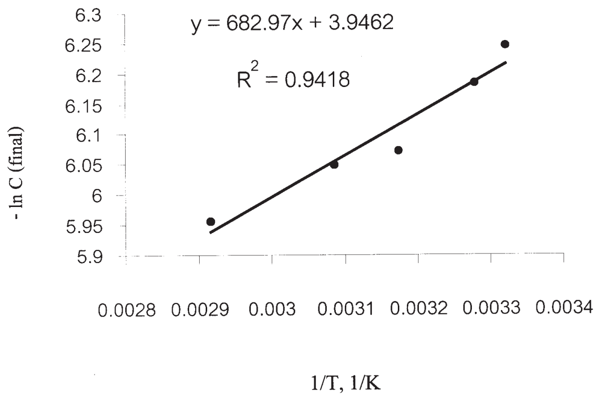

Figure 8. Clausius-Clapeyron plot at various temperatures for adsorption of iron ion on activated carbon obtained from coconut shell.

Table 2. The maximum adsorption of iron ion at monolayer coverage (X_{max}) and the heats of adsorption (ΔH_{ads}) for iron ion on three types of activated carbons with a sample to $ZnCl_2$ ratio, 1:3 and activation temperature at 600 °C.

Raw material	X_{max} (mmol iron/g)	ΔH_{ads} (kJ/mol)
Bagasse	0.66	-8.9
Pericarp of rubber fruit	0.41	-9.7
Coconut shell	0.19	-5.7

The heat of adsorption was calculated from the slope of those straight lines. The numerical value of Langmuir isotherm constant for the maximum adsorption at monolayer coverage (X_{max}) and the heats of adsorption (ΔH_{ads}) of iron ion on three types of activated carbons with a sample to $ZnCl_2$ ratio, 1:3 at 600 °C was summarized in Table 2.

Acknowledgments

This research was supported by Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, and partially supported by the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry. The authors would like to thank Department of Mining and Material Engineering and Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, for kindly giving permission to use a 325 mesh sieve and a thermostat shaker bath.

References

Alberty, R.A. and Silbey, R. J. 1992. Physical Chemistry. 1st edition. John Wiley & Sons, Inc., New York. pp. 187.

American Standard of Testing Material. 1999. "Standard Test Method for Determination of Iodine Number of Activated Carbon". Annual book of ASTM sec. 15, vol. 4, D4607-94.

Chaiwattananont, R., Niyomwan, N. and Noda, Y. 1998. Optimum condition for high quality activated carbon production from Thai raw materials. Report no. 6, Thailand Institute of Scientific and Technological Research.

Ferro-Garcia, M.A., Rivera-Utrilla, J., Rodriguez-Gordillo and Bautista-Toledo, I. 1988. Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. Carbon. 26: 363-373.

Hassler, J.W. 1974. "Purification with Activated Carbon: Industrial Commercial Environmental". Chemical Publishing Co., Inc., New York. pp. 172.

Huang, C.P. and Blankenship, D. W. 1984. The removal of mercury(II) from dilute aqueous solution by activated carbon. Water Res. 18: 37-46.

Manahan, S.E. 1991. Environmental Chemistry, 5th edition, Lewis Publishers, Inc., Michigan. pp. 200.

Shaw, D.J. 1980. Introduction to Colloid and Surface Chemistry. 3rd edition. Butterworth & Co (Publishers) Ltd, London. pp.118.

Tanada, S., Kawasaki, N., Nakamura, T., Araki, M. and Tachibana, Y. 2000. Characteristics of nonafluorobutyl methyl ether (NFE) adsorption onto activated carbon fibers and differet-size-activated carbon particles. J. Colloid Interface Sci. 228: 220-225.

Uchida, M., Shinohara, O., Ito, S., Kawasaki, N., Nakamura, T. and Tanada, S. 2000. Reduction of iron(III) ion by activated carbon fiber. J. Colloid Interface Sci. 224: 347-350.

Vitidsant, T., Suravattanasakul, T. and Damronglerd, S. 1999. Production of activated carbon from palm-oil shell by pyrolysis and steam activation in a fixed bed reactor. ScienceAsia. 25: 211-222.

Wan Ngah, W.S. and Liang, K.H. 1999. Adsorption of gold(III) ions onto chitosan and n-carboxymethyl chitosan: equilibrium studies. Ind. Eng. Chem. Res. 38: 1411-1414.