

A Review Of Activated Carbon By Chemical Activation

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Abstract – This study discussed the basics of Adsorption such as Adsorption Process, Classification, Techniques and Isotherms. The detailed discussions about the factors influencing Adsorption were carried out. The association of all the factors which affect the Adsorption process (physical and chemical), Adsorbent and Adsorbate with Adsorption were also discussed. The historical backgrounds behind those parameters were also tabulated. The detailed study about the Surface properties of various Activated Carbons was carried out. Surface area and Pore volumes of different Activated Carbons were obtained and comparisons were done.

Keywords: Activated Carbon, Adsorption, Chemical Activation.

1. INTRODUCTION

Many physical and chemical processes occur at different interfaces. Adsorption is one of the main and basic surface phenomena. It is a spontaneous accumulation of Adsorbate at the solid surface of the adsorbent. Adsorbent is solid on which adsorption occurs. Adsorbate is a substance which is adsorbed on a solid surface. In water treatment, Adsorption has been proved as an efficient removal process for multiplicity of solutes. In the bulk material, all the bonding requirements (ionic, covalent or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates.

1.1 ADSORPTION

The Adsorption process is generally classified as either *Physisorption* (Physical Adsorption) or *Chemisorption* (Chemical Adsorption). Physisorption is adsorption in which the forces involved are intermolecular forces (Van der waals force), hydrogen bonding and Ion exchange process. Chemisorption is adsorption in which the forces involved are valence forces / chemical bonds. Adsorption may be classified into different manners such as Localized, Nonlocalized, Negative – Positive, Static – Dynamic, etc., when solute is adsorbed by an adsorbent, it is called Positive Adsorption. But the solvent is taken up by the adsorbent it is called Negative Adsorption. The experimental techniques for studying adsorption can be divided into three classes. They are, Techniques based on the measurement changes in the electrical, magnetic and work function properties of solid adsorbent during adsorption, Techniques based on the study of radiation, electrons and ions with the adsorbed layer and Spectroscopic methods.

An *Adsorption Isotherm* for an adsorbate on a solid is the function which relates at constant temperature, the amount of substance adsorbed at equilibrium to the pressure (or concentration) of the adsorptive in the gas phase. *Adsorption Isobar* The function relating the amount, mass or volume, or corresponding excess of substance adsorbed by a given amount of solid, to the temperature at constant pressure. *Langmuir Isotherm* assumes that a single adsorbate binds to a single site on the adsorbent and that all surface sites on the adsorbent have the same affinity for the adsorbate. *Freundlich Isotherm* assumes that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir Isotherm. *BET Isotherm* assumes that a number of layers of adsorbate accumulate at the surface and that the Langmuir Isotherm applies to each layer.

There are many factors which influence the Adsorption process. A rise in *Temperature* increases the kinetic energies of solute particles and hence these particles leave the surface and thereby lowering the extent of adsorption. Also at low temperatures, the Adsorbate molecules have insufficient kinetic energy to enter the pores. At low temperature, the extent of adsorption increases rapidly with *Pressure* and decreasing adsorbing energies. Greater the *Surface Area*, more is the surface available for adsorption and smaller the particle size, greater its surface area. A decrease in *Pore Size* increased the Adsorption because of high specific sorption sites and the contact points between Adsorbate and Adsorbent surface increased. For Micropores, entire volume can be considered as the adsorption space and for macropores and mesopores, the layer by layer adsorption mechanism is accepted. *Nature of the Adsorbent* such as Porous, rough surface and finely powdered solids adsorb more. Adsorption is more

when the *Molecular Weight* of the solute is high. When the electrostatic forces between the Adsorbent surface and Adsorbate ions are attractive, an increase in *Ionic Strength* will decrease the adsorption capacity. At low *pH*, high electrostatic attraction between positive charged Adsorbent and Adsorbate. If *pH* is less than *Zero Point Discharge* (*pHzpc*), Adsorbent surface becomes suitable for adsorption of positive ions and if *pH* is greater than *pHzpc*, Adsorbent surface becomes suitable for adsorption of negative ions. The increase in *Adsorbent Mass* increases the contact surface of Adsorbent particles which means that it will be more probable for solute molecules to be adsorbed on adsorption sites. Greater *Solubility of Adsorbate* provides stronger binding between Adsorbate and Adsorbent. A material which has low solubility in water will show higher affinity with solid surfaces than water. Increased in *Salinity* generates a compressed electrical double layer which exerted repulsive force, retarding the adsorption. *Activation* increased the surface area thereby increased the Adsorption. With the increasing of the *Agitation Speed*, the rate of diffusion of the molecules to the surface of the Adsorbent becomes higher because of an enhancement of the turbulence.

1.2 ACTIVATED CARBON

Activated Carbons (AC) can be produced from different carbon containing raw materials and by different activation processes. It is prepared by heating the raw materials to drive off the hydrocarbons. Then it is carbonized by the process of *Carbonization*, which is necessary to transform the cellulose structure into carbonaceous material. Such cellulose structures contain a number of oxygen and hydrogen containing functional groups, which can be removed by dehydrating chemicals. Followed by *Activation*, is the process of heating the adsorbents with the particular temperature and time. There were generally two kinds of Activation. *Physical Activation* involves carbonization of a carbonaceous followed by activation in presence of CO_2 or steam. The raw material is brought in contact with an activation gas at elevated temperatures. During the activation, the activation gas reacts with the solid carbon to form gaseous products. *Chemical Activation* involves carbonization of a carbonaceous followed by activation in presence of chemicals such as ZnCl_2 and H_3PO_4 . The process of transformation of cellulose structure into a carbonaceous material by dehydration at elevated temperatures under pyrolytic conditions was carried out. *Regeneration* of Activated Carbon is the process which describes all the processes that are used to recover the adsorptive capacity of the spent carbon. *Reactivation* is the process used to create the activated carbon from virgin material by oxidizing the adsorbed organic material and thus removing it from the carbon surface.

2 MATERIALS

2.1 NORIT C-granular (Nc) & Carbon Black (Cbk) – It was prepared from wood by chemical activation using Phosphoric acid. Nc was heated in a flow of ultra high purity N_2 to 500°C , 650°C , 800°C , 875°C & 950°C for 3 hrs. Carbon Black was subjected to heat treatment in H_2 at 950°C .

2.2 NORIT ROX – It was prepared by Chemical Activation of Activated carbon, pellets of 0.8mm diameter and 5mm length, using nitric acid & H_2O_2 . Nitric acid activation carried at Boiling Temperature for 6 hrs or H_2O_2 activation carried at room temperature. The material was oxidized in gas phase with O_2 and oxidized in liquid phase with distilled water.

2.3 Palm Shell – It was obtained from Malaysia oil palm shell, of particle size 1-2mm, by chemical activation using K_2CO_3 . It was dried in an oven at 110°C for 24 hrs. It was then activated from 600°C to 1000°C with the duration of 2hrs.

2.4 AC with lignin – It was prepared from Kraft pulping of wood by chemical activation using K_2CO_3 , Na_2CO_3 , KOH , NaOH , ZnCl_2 & H_3PO_4 . It was heated under N_2 at the rate of 10°C for 1 hr with the temperature of 500°C to 900°C .

2.5 Cassava peel – It was prepared by chemical activation using KOH . Carbonization and activation was performed under N_2 flow at the rate of $10^\circ\text{C} / \text{min}$ with the temperatures of 450°C , 550°C , 650°C and 750°C for 1hr, 2hrs or 3hrs. It was dried at 110°C for 24hrs.

2.6 Almond shell – It was prepared at 1173K in a N_2 flow for 1 hr and activated at 1123K. It was oxidized with HNO_3 , H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 1hr, 2.5hr, 5hr and 8hr.

2.7 Almond shell, Hazelnut shell & Apricot stone – They were prepared by chemical activation using ZnCl_2 . They were dehydrated at 103°C for 6-10-18-24hrs and activated at 750 - 800 - 850°C for 2hrs under N_2 flow at the rate of 40ml/min. They were dried at 110°C for 24hrs.

2.8 Bituminous Coal – It was prepared from bituminous coal by chemical activation using KOH or ZnCl_2 . It was heated at the rate of $15^\circ\text{C}/\text{min}$ to 800 or 900°C in a N_2 flow. It was then dried at 100°C for about 14hrs.

2.9 Coal & Wood based Carbon – Thermally activated coal based carbon (Calgon F400) and acid activated wood based carbon (Westvaco WVB) were oxidized using HNO_3 in a flow of N_2 at 1000°C for 24hrs.

2.10 Columbia Carbon & Black Pearls – They were oxidized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and reduction with concentrated HCl. They were dried at 110°C for 12hrs.

2.11 Sugarcane Bagasse, Rice hulls, Rice straw & Pecan shell – They were pyrolyzed in a N_2 flow at 750°C for 1hr with H_3PO_4 . They were dried at 50°C for 12hrs.

2.12 Plum Kernel – It was prepared by chemical activation using NaOH under N_2 flow at 780°C for 1hr. Carbonization was carried at 450°C for 2hrs.

2.13 Coir pith – It was prepared by chemical activation with ZnCl_2 at 700°C for 1hr. It was dried at 60°C for 12hr. Carbonization was done with H_2SO_4 , HCl, HNO_3 and H_3PO_4 for 24hrs. It was dried at 80°C for 6hrs.

3 DISCUSSIONS

It was discussed that the physical and chemical activation helps to improve the adsorptive capacity of the various Activated Carbons by changing the nature of the parameters like Surface area, Micropore volume, oxidation, carbonation, and impregnation etc., Table 1 shown the detailed discussion of surface modifications of various Activated Carbons using various chemicals. The Surface areas and Micropore volumes of Activated Carbons were also mentioned in Table 1. Carbonization temperature, Activation time and impregnation ratios of the activation process for which the surface areas and micropore volumes of the activated carbons are so high were also discussed. The activation temperatures of all the activated carbon were about 500°C to 900°C but the activation time varies from 1 hr to 24 hrs.

All the activated carbons mentioned were rich in carbon content. While activating these activated carbons with the help of the chemicals mentioned, the properties were changed thereby adsorptive capacity also increased. Most used chemicals were HNO_3 , K_2CO_3 , Na_2CO_3 , KOH, H_2O_2 , NaOH, ZnCl_2 , H_3PO_4 & $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Physical activation was also carried out for some of the activation carbons with the help of CO_2 . Treatment with N_2 was also carried out to increase carbon basicity by removing surface oxygen.

The comparisons of activated carbons with different parameters are given in Fig 1 and Fig 2. Fig 1 shows that the variations of surface areas of various Activated carbons. Activated Carbon from lignin activated with K_2CO_3 produced the surface area of $2000\text{m}^2/\text{g}$ because K_2CO_3 modifies the carbonation behavior of the lignin as a chemical reagent in two temperature ranges, below 500°C and above 600°C . Fig 2 shows that the variations of micropore volume of various Activated carbons. Acid washed wood based Activated Carbon produced the micropore

volume of $1.357\text{ cm}^3/\text{g}$ because Oxidation in HNO_3 increased the acidity by creating the new carboxylic, lactonic and phenolic type of functionalities.

The following figures, the activated carbons prepared with chemical activation were indicated as abscissa. 1 to 17 indicated the activated carbons which were shown in the Table 1.

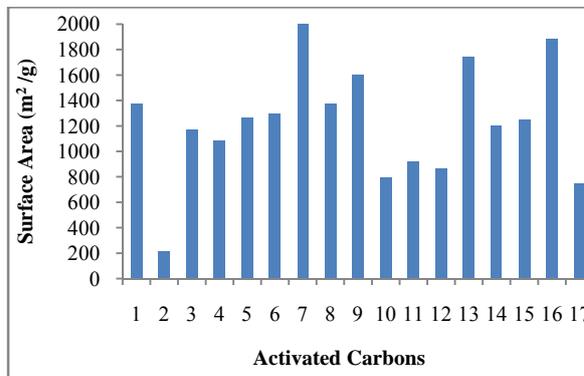


Fig.1. Variations of Activated Carbons Vs Surface area

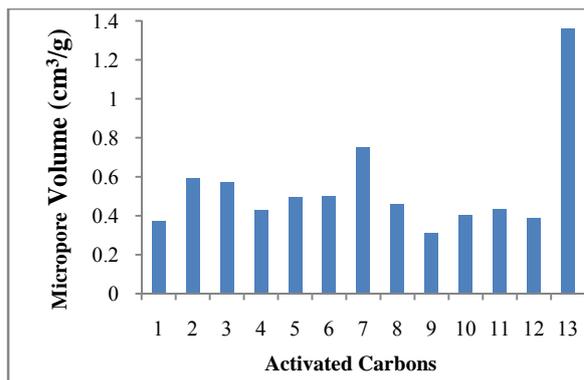


Fig.2. Variations of Activated Carbons Vs Micropore Volume

It was clearly indicated that the adsorptive capacity was increased by modifications in the surface area and micropore volume. Carbonation temperature plays the major role in activation process because the free ions present in the surface were liberated at the particular temperature and followed by the chemical activation increases the adsorptive power of stronger bonds in the activated carbons, thereby adsorption was increased.

S. No.	Activated Carbon	Surface area (m ² /g)	Micro pore volume (cm ³ /g)	Carbonization Temp (°C)	Discussions	Remarks
1.	NORIT C-granular AC	1378	0.37	950	<ul style="list-style-type: none"> • There is no change in the physical properties of Nc. • There is a significant increase in surface area of Cbk. • Values of IEP and PZC are low. • Presence of acidic surface groups in the surface of the carbon. • The resultant surface is very active. • External oxidation takes place. • The ratio of external to internal surface area is low for Nc. • The ratio of external to internal surface area is low for Cbk. 	-
2.	NORIT AC oxidized with 50% N ₂ O	217	0.592	500	<ul style="list-style-type: none"> • There is no change in the texture of Activated Carbon. • Under drastic conditions, there is a decrease in surface area and pore volume while the average micro pore width increases, due to collapse of the pore walls. • There is an increase in oxygen content. • Oxidation increases the concentration of hydroxyl + anhydrides and carboxylic groups. • It increases CO₂ evolution at low temperatures. 	Activation time 8hrs
3.	AC with K ₂ CO ₃	1170	0.57	800	<ul style="list-style-type: none"> • Surface area and micropore volume are increased from 600°C to 800°C and then decreased. • Surface area increases with increase in impregnation ratio from 0.5 to 1 and then decreases from 1 to 2. • Increase in impregnation ratio decreased the density of AC and Increase in carbonation temperature increased the density of AC. • The increase in carbonation temperature and impregnation ratio decreased yield and increased the product adsorption capacity of CO₂. 	Impregnation ratio 1:1
4.	Coal AC	1089	0.428	-	<ul style="list-style-type: none"> • The Surface area is maximum at temperature of 800°C in alkali metal compound activation and at the temperature of 600°C with ZnCl₂, H₃PO₄. 	-
5.	Coconut shell AC	1267	0.492	-		-

S. No.	Activated Carbon	Surface area (m ² /g)	Micro pore volume (cm ³ /g)	Carbonization Temp (°C)	Discussions	Remarks
6.	AC from lignin with ZnCl ₂	1300	0.5	600	<ul style="list-style-type: none"> The carbon prepared by K₂CO₃ activation has a surface area being much larger than that of the commercial activated carbon. 	Impregnation ratio 1:1
7.	AC from lignin with K ₂ CO ₃	2000	0.75	800	<ul style="list-style-type: none"> The pore volumes increased with an increase in temperature over the range 500°C to 600°C in ZnCl₂, H₃PO₄ and at the temperature 800°C. K₂CO₃ modifies the carbonation behavior of the lignin as a chemical reagent in two temperature ranges, below 500°C and above 600°C, while ZnCl₂ modifies below 600°C. 	Impregnation ratio 1:1
8.	AC from Cassava peel	1378	0.46	750	<ul style="list-style-type: none"> Surface area and pore volume were increased with increase in carbonization time and temperature. The micropore volume increased upto 650°C because of widening of the spaces between the carbon atomic layers. When the temperature was above 650°C, micropore volume was decreased because the surface metal is responsible for further carbon gasification, leading to widening of micropore to mesopore. 	Impregnation ratio 1:1
9.	AC from Almond shell	1600	0.309	850	<ul style="list-style-type: none"> Surface area and pore volume were increased with increase in activation time Activated carbon treated with HNO₃ decreases the surface area and pore volumes than the original Activated carbon since an increase in degree of activation makes the pore walls thinner and more easily destroyed. Activated carbon treated with H₂O₂ & (NH₄)₂S₂O₈ were produced the same surface area and pore volume as the original Activated carbon and in some cases, there were constrictions due to the fixation of oxygen surface complexes at the entry of the micropore. 	Activation time 8hrs
10.	AC from Hazelnut shell	793	0.4	750	<ul style="list-style-type: none"> Surface area of Activated carbon was increased with activation and time. Highest Surface area of AC from Almond shell, Hazelnut shell and Walnut shell were produced at 750°C with 10hr 	Activation time 10hrs

S. No.	Activated Carbon	Surface area (m ² /g)	Micro pore volume (cm ³ /g)	Carbonization Temp (°C)	Discussions	Remarks
					activation but for apricot stones it was obtained at 800°C with 18hr activation time. <ul style="list-style-type: none"> Carbon contents were also increased for all the Activated carbons. 	
11.	Bituminous coal with KOH	925	0.431	700	<ul style="list-style-type: none"> Surface area and micropore volume were increased with increase in carbonization time and temperature for KOH activation. 	Impregnation ratio 1:2
12.	Bituminous coal with ZnCl ₂	865	0.388	500	<ul style="list-style-type: none"> In ZnCl₂ activation, Surface area and micropore volume were decreased with increase in carbonization time and temperature. 	Impregnation ratio 1:1.2
13.	Acid Washed Wood Based AC	1745	1.357	-	<ul style="list-style-type: none"> Surface area and pore volume were not changed for the coal based carbon, whereas for wood based carbon, surface area and pore volume were decreased. Oxidation in HNO₃ increased the acidity by creating the new carboxylic, lactonic and phenolic type of functionalities. 	-
14.	Columbia Carbon (LC325)	1200	-	-	<ul style="list-style-type: none"> Surface area of LC325 was decreased upon Oxidation and Reduction treatment whereas for P607 little changes were observed. LC325 developed a large amount of surface acidity and the adsorptive capacity of the carbon reduced. 	-
15.	AC from pecan shell with 50% H ₃ PO ₄	1250	-	450	<ul style="list-style-type: none"> Surface area was increased with increase in amount of chemicals and activation time. Carbons obtained by physical activation had lower surface areas than carbons obtained by chemical activation. Chemical activation is carried out at lower temperatures than physical activation. Carbon produced at power temperatures is likely to possess an extensive surface area and a well developed microporosity. 	Activation time 1hr
16.	AC from plum kernels	1887	-	780	<ul style="list-style-type: none"> Surface and pore volume were first decreased with NaOH/char ratio then increased significantly. Surface pyrolysis and NaOH etching occurred in the activation process, but only on the surface. 	Weight NaOH/char ratio is 4

17.	AC from Coir pith	752	-	700	<ul style="list-style-type: none"> • Surface area was increased with increase in carbonization temperature and increase in impregnation ratio. • In ZnCl₂ activation method, increasing impregnation ratio increased the percent yield. 	Impregnation ratio 1:1

Table 1
Modifications of the Surfa

ce Chemistry of various Activated Carbons

4. CONCLUSION

It was concluded that physical and chemical activation improved the adsorptive capacity of the Activated carbons. The Surface areas of chemically activated carbons were larger than the activated carbon. The Micro pores were also well developed. Activated Carbon from lignin activated with K_2CO_3 produced the surface area of $2000m^2/g$. Acid washed wood based Activated Carbon produced the micropore volume of $1.357 cm^3/g$. Also carbonization temperature and impregnation ratio produced significant effect in the pores of the activated carbon. Comparing physical and chemical activation indicated that the chemical activation was more flexible in the preparation of activated carbons.

REFERENCE

1. A K Bajpai and M Rajpoot. Adsorption Techniques – A Review.
2. A.Ahmadpour, D.D.Do. The preparation of Active carbons from Coal by Chemical and Physical Activation.
3. A.Aygun, S.Yenisoy-Karakas, I.Duman. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties.
4. Arlette M. Cardenas-Peña, Jorge G. Ibanez*, Ruben Vasquez-Medran. Determination of the Point of Zero Charge for Electrocoagulation Precipitates from an Iron Anode.
5. Bengt Kronberg and Per Stenius. The Effect of Surface Polarity on the Adsorption of Nonionic Surfactants
6. C.Moreno-Castilla, M.A.Ferro-Garcia, J.P.Joly, I.Bautista-Toledo, F.Carrasco-Marin, J.Rivera-Utrilla. Activated Carbon Surface Modifications by Nitric acid, Hydrogen Peroxide and Ammonium Peroxydisulfate Treatments.
7. C.Namasivayam, K.Kadirvelu. Activated Carbons Prepared from Coir Pith by Physical & Chemical Activation Methods
8. Clair N.Sawyer, Perry L.McCarty and Gene F.Parkin. Chemistry for Environmental Engineering and Science.
9. Donni Adinata, Wan Mohd Ashri Wan Daud, Mohd Kheireddine Aroua. Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3 .
10. Eckhard Worch. Adsorption Technology in Water Treatment.
11. Fusheng Lia,*, Akira Yuasab, Kunio Ebiec, Yoshihiro Azumad, Takashi Hagishitae, Yoshihiko Matsui. Factors affecting the adsorption capacity of dissolved organic matter onto activated carbon: modified isotherm analysis.
12. G.Alagumuthu, V.Veeraputhiran, R.Venkatraman. Adsorption Isotherms on fluoride removal : Batch techniques.
13. George Tchobanoglous, Franklin L.Burton, H.David Stensel. Wastewater Engineering – Treatment and Reuse.
14. H. I. Maarof, B. H. Hameed and A. L. Ahmad. Aqueous-Phase Adsorption of Phenolic Compounds on Activated Carbon.
15. J.Angel Menendez, Jonathan Phillips, Bo xia, Ljubisa R.Radovic. On the Modification and Characterization of Chemical Surface Properties of Activated Carbon: In the search of Carbons with Stable Basic Properties.
16. J.L.Figueiredo, M.F.R.Pereira, M.M.A.Freitas, J.J.M.Orfao. Modification of the surface chemistry of activated carbons.
17. Jun'ichi Hayashi, Atsuo Kazehaya, Katsuhiko Muroyama, A.Paul Watkinson. Preparation of activated carbon from lignin by chemical activation.
18. Krzysztof Kus'mierek1 Andrzej S'wia, tkowski. The influence of different agitation techniques on the adsorption kinetics of 4-chlorophenol on granular activated carbon.
19. Lei Li, Patricia A. Quinlivan, Detlef R.U. Knappe. Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution.
20. M.Ahmedna, W.E.Marshall, R.M.Rao. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties.
21. Minguang Dai. The effect of Zeta potential of Activated Carbon on the Adsorption of Dyes from Aqueous Solution.
22. O.F. Okeola*, E.O. Odebunmi and O.M. Ameen. Comparison of Sorption Capacity and Surface Area of Activated Carbon prepared from Jatropha Curcas Fruit Pericarp and Seed coat.
23. Paweł Kempisty1, Paweł Strak1, Konrad Sakowski1, Stanisław Krukowski. Energy of adsorption at semiconducting surfaces with Fermi level differently pinned - ab initio study
24. Pimol Punjongharn1, Khanidtha Meevasana2, Prasert Pavasant. Influence of particle size and salinity on adsorption of basic dyes by agricultural waste: dried Sea grape (Caulerpa lentillifera).
25. Robert W.Coughlin and Fouad S.Ezra. Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon.
26. Ru-Ling Tseng. Physical and Chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation.
27. Tanju Karanfil, James E Kilduff. Role of Granular Activated carbon Surface Chemistry on the Adsorption of Organic Compounds.
28. Xin Jin, Kui Chen, Jia-wen Zhu, and Yan-yangWu. Effect of Solution Polarity and Temperature on Adsorption Separation of Erythromycin A and C onto Macroporous Resin SP825.
29. Y.Sudaryanto, S.B.Hartono, W.Irawaty, H.Hindarso, S.Ismadji. High surface area activated carbon from cassava peel by chemical activation.
30. Yahya S. Al-Degs a, Musa I. El-Barghouthi a, Amjad H. El-Sheikh a, Gavin M. Walker b. Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon.