
MODIFICATION OF THE SURFACE CHEMISTRY OF ACTIVATED CARBON AND ITS INFLUENCE ON METHYLENE BLUE ADSORPTION

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Abstract

The adsorption behavior of activated carbons is determined not only by their porous structures but also by the chemical nature of its surface. The surface chemistry of activated carbons can be selectively modified in order to improve their adsorption capacity. In this study, a NORIT granular activated carbon was treated by oxidant (HNO_3) and non-oxidant acid (HCl) at different concentrations and temperatures. The surface chemistries of the materials were characterized by Boehm titration method and by the determination of the point of zero charge (pH_{pzc}). The adsorption properties of the selected samples were studied by adsorption of methylene blue, which is one of the important dyes and found in many textile effluents. In addition, the pore structures of the modified carbons were also studied by argon adsorption at 87.29 K. As results, it was observed that both HNO_3 and HCl treatments could increase the surface acidity of activated carbons. Activated carbons modified by HCl gave the best performance on the adsorption of methylene blue.

Keywords: Activated Carbon, Surface Chemistry, Chemical Treatment, Boehm Titration Method, Adsorption

Abstrak

Kemampuan adsorpsi karbon aktif tidak hanya ditentukan oleh struktur pori tetapi juga dipengaruhi oleh sifat kimia dari permukaannya. Sifat kimia permukaan karbon aktif dapat secara selektif dimodifikasi dengan tujuan untuk lebih meningkatkan kapasitas adsorpsinya. Pada penelitian ini, karbon aktif NORIT granular ditreatment dengan menggunakan asam oksidator (HNO_3) dan non-oksidator (HCl) pada berbagai konsentrasi dan suhu. Sifat kimia permukaan karbon aktif dikarakterisasi dengan menggunakan metode titrasi Boehm serta dengan penentuan point of zero charge (pH_{pzc}). Kemampuan adsorpsinya diuji dengan mengadsorp larutan methylene blue, dimana methylene blue merupakan salah satu komponen dalam limbah tekstil. Sedangkan struktur pori karbon aktif dianalisa dengan adsorpsi Ar pada suhu 87,29 K. Penelitian ini menunjukkan bahwa baik treatment dengan HNO_3 maupun HCl dapat mengakibatkan terjadinya peningkatan sifat asam pada permukaan karbon aktif. Karbon aktif yang diberi perlakuan dengan HCl memberikan kemampuan adsorpsi yang paling baik dalam adsorpsi larutan methylen biru.

Kata Kunci: Karbon Aktif, Sifat Kimia Permukaan, Perlakuan dengan Larutan Kimia, Metode Titrasi Boehm, Adsorpsi

1. Introduction

Activated carbons have been widely used in many separation processes such as gas separation, water purification, and removal of color, odor, and organic pollutant from wastewater. They are the most commonly used as adsorbent due to their high specific surface area as well as adsorption capacity (El-Sayed and Bandosz, 2004; Park *et al.*, 2003).

The adsorption behaviour of activated carbons is determined not only by their porous structures (specific surface area and pore size distribution) but also by the chemical nature of its surface (Benaddi *et al.*, 2000; El-Sayed and Bandosz, 2003; Garcia *et al.*, 2004; Rodriguez-Reinoso, 1998). The porous structure of carbon determines its adsorption capacity, while its surface chemical groups affect its interaction with polar and non polar adsorbates (Park *et al.*, 2002). Pereira *et al.* (2003) studied the influence of surface chemical groups on dyes removal. They modify surface chemistry of activated carbon without changing significantly its textural properties. It is found that activated carbons with different surface chemistries can lead to different amount of dyes removed. This research indicates that surface chemistry of activated carbon can play a dominant role in the adsorption processes.

The adsorption capacities of activated carbons on specific compounds also depend on the carbon surface chemical features (Rioz *et al.*, 2003). Therefore, the surface chemical modification is of great interest, which can improve their adsorption capacity and selectivity on certain adsorbate in gaseous or liquid phase. A thorough knowledge of activated carbon surface chemistry enables the preparation of adsorbent with appropriate characteristic for specific application. Some progresses have been made in the development and modification of surface chemistry of carbons. Therefore, in using carbons as adsorbent for specific application, we need to know the surface characteristic of the carbons.

Detail characterization of modified activated carbon is essential to understand phenomenon occur during treatment process. The understanding of the amount and types of surface functions created and the change of surface area and the pore structure during modification is crucially important because these factors also affect the ability of carbon to adsorb gaseous and liquid species. Several authors (Figueiredo *et al.*, 1999; Laszlo *et al.*, 2001; Lopez-Ramon, 1999) have investigated various techniques of the characterization of activated carbons' surface chemistry.

The surface characteristics of activated carbons (porosity and surface chemistry) depend on the origin of the precursor and method of activation (El-Sayed and Bandosz, 2003). The activation on the same raw material with different method can produce totally different carbon characteristics (Park *et al.*, 2002). Therefore, activated carbon used in this study is limited to one material, which was produced from coconut shell with chemical activation. This carbon, then, was treated with non-oxidant (HCl) and oxidant acid (HNO₃) at different concentrations and temperatures to yield series of modified activated carbons.

The main objectives of the present work were to modify the carbon surface chemistry and to characterize the carbon surface chemistry. The performance of activated carbons before and after treatment was tested for removal of methylene blue, which is one of the common dyes found in the textile effluent.

2. Fundamental

The carbon matrix does not consist of carbon atoms alone, but also formed by other heteroatom like hydrogen, oxygen, nitrogen, halogen, sulfur, phosphorus, etc. (Do, 1998; Laszlo *et al.*, 2001). These heteroatom bonded to the edges of the carbon layers, which govern the surface chemistry of activated carbon (Aygün *et al.*, 2003; El-Sayed and Bandosz, 2004). The origin of these surface groups may be derived from the original raw material, the activation process or introduction after preparation via post treatment (Benaddi *et al.*, 2000; Rodriguez-Reinoso, 1998).

The surface chemistry of carbon materials is basically determined by the acidic and basic character on their surface. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, aldehyde, quinone, hydroquinone, cyclic peroxide, etc., has been postulated as constituting the source of surface acidity (Boehm, 1994; Henning *et al.*, 1989; Laszlo *et al.*, 2001; Park *et al.*, 2002; Yang, 2003). Whereas the basic properties of activated carbon is associated with two types of structures: (i) the presence of oxygen containing groups, i.e. pyrone, chromene and carbonyl structures, at the edge of carbon crystallite; and (ii) oxygen free Lewis basic site on the graphene layers. The Lewis basicity of delocalized π electrons is influenced by the aromatic system on carbon surface (Boehm, 1994; Laszlo *et al.*, 2001; Leon y Leon *et al.*, 1992; Pereira *et al.*, 2003; Yang, 2003).

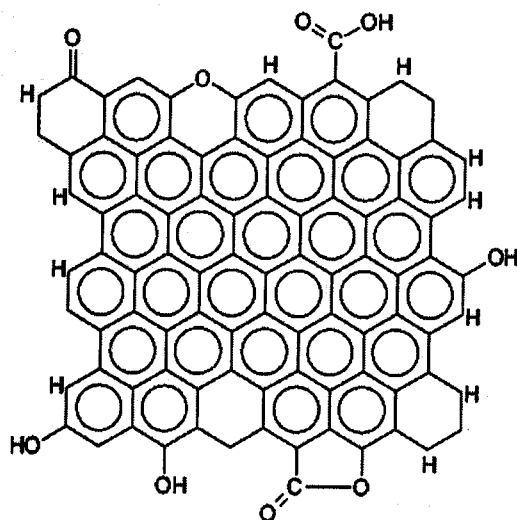


Figure 1. Some Types of Oxygen Functional Groups in Activated Carbon

The surface acidity/basicity depends on the amount and types of surface functional groups. Different functional groups on carbon surface are responsible for the amphoteric nature of carbon. Consequently, both negatively and positively charged surface sites exist in aqueous solution, depending on the pH (Radovic *et al.*, 1997; Rodriguez-Reinoso, 1998). At some pH, the carbon surface charge will be zero; this is so-called point of zero charge (pH_{pzc}). At $pH_{pzc} < pH$, carbon surface becomes negatively charge favouring the adsorption of cationic species. On the other hand, adsorption of anionic species will be favoured at $pH_{pzc} > pH$ (Radovic *et al.*, 1997; Yang, 2003).

Modification of the surface chemistry of activated carbon can be carried out through liquid phase treatments at different temperatures, concentrations and/or contact times. Many reagents can be used, such as HNO_3 , H_2O_2 , $(NH_4)_2S_2O_8$, H_2SO_4 , $NaOCl$, bichromate, permanganate, NH_3 (Faria *et al.*, 2004; Moreno-Castilla *et al.*, 2000; Pereira *et al.*, 2003; Rios *et al.*, 2003), HF , HCl (Moreno-Castilla *et al.*, 1998) etc. Other treatments are gas phase oxidation with O_2 or N_2O at different temperatures, pressures, concentrations and/or contact times; and heat treatments at different temperatures to selectively remove some of the functional groups (Pereira *et al.*, 2003).

Classical acid/base titration proposed by Boehm *et al.* in 1966 (Boehm, 1994) are applied in our research to characterize the surface chemistry of activated carbon. This method differs with the others because it can quantify the equivalent of surface acidic oxides and basic groups on the carbon surface. Boehm titration method uses

$NaOH$, Na_2CO_3 and $NaHCO_3$ as reagents to account the surface acidity whereas the determination of surface basic sites uses HCl . The amount of acidic groups on the activated carbon is calculated under the assumption that $NaOH$ neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 , carboxylic and lactonic; $NaHCO_3$, only carboxylic group. The number of surface basic sites is calculated from the amount of HCl that reacted with the carbon. The reaction between the reagents and the acidic oxygenated-functional groups on the surface is based on the difference in acid/base strength. The strength of acidic groups is as follow (Boehm, 1994): carboxyl > lactone > phenol.

3. Experimental

A NORIT granular activated carbon purchased from PT Bratako Chemika (Surabaya) was used as the parent carbon. Other chemicals used in this study were HNO_3 (65%, $\rho = 1.4 \text{ gr/cm}^3$, $Mr = 63.01$), HCl (37%, $\rho = 1.19 \text{ gr/cm}^3$, $Mr = 36.5$), $NaHCO_3$ p.a. ($Mr = 84.01$), Na_2CO_3 p.a. ($Mr = 106$), $NaOH$ p.a. ($Mr = 40$), $H_2C_2O_4 \cdot 2H_2O$ p.a. ($Mr = 126.03$), $Na_2B_4O_7 \cdot 10H_2O$ p.a. ($Mr = 381.37$), $NaCl$ p.a. ($Mr = 58.5$), Methylene Blue ($Mr = 319.86$).

Prior to experiments, the parent carbon was washed with distilled water to remove water-soluble compounds and then dried in an oven (Duo-vac oven, Lab-Line Instruments Inc.) at $110^\circ C$ until it reached constant weight. After that, it was stored in a dessicator (sample AC1).

For the treatment with HNO_3 , about 12 g of AC1 was mixed with HNO_3 solution with concentration of 3, 6, 9, and 12 M. The mixture then maintained at $30^\circ C$ using water bath (Memmert W-350) for 4 h. This treatment is repeated for other variation of temperatures (60° and $80^\circ C$). Subsequently all samples were washed thoroughly with distilled water to neutral pH and then dried. Finally, the samples were collected and stored in a dessicator. Treatment with HCl was carried out in a similar way with HNO_3 treatment as described above.

The acidity and basicity of all activated carbons samples were determined by Boehm titration method (Boehm, 1994). The Boehm method is described as follow: 0.5 g of carbon sample was added to a series of Erlenmeyer containing 50 cm^3 of 0.05 N: $NaOH$, Na_2CO_3 , $NaHCO_3$, and HCl solutions. The Erlenmeyer were then sealed and shaken for 24 h at room temperature. Then the suspension was decanted and 10 cm^3 of the remaining solution was titrated

with 0.05 N HCl or NaOH, depending on the original solution used. The pH_{PZC} of five samples were determined using pH drift method. The procedure of pH_{PZC} determination can be described as follows (Faria *et al.*, 2004): 50 cm³ of 0.01 N NaCl solution was placed in a closed Erlenmeyer. The pH was adjusted to value between 2 and 12 by adding HCl 0.1 N or NaOH 0.1 N solutions. Then, 0.15 g of each activated carbon sample was added and the final pH measured after 48 h (using pH meter Schott CG 825) under agitation at room temperature. The pH_{PZC} is the point where the curve pH_{final} vs $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$.

Preliminary experiments were made in order to obtain a maximum absorption wavelength of methylene blue solution and the time necessary to achieve the equilibrium condition (4 days).

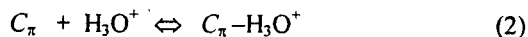
For the adsorption experiments, five samples of activated carbon (modified and parent) were used as adsorbent. Different amounts of carbon (0.1; 0.3; 0.5; 0.7; 0.9; 1.1 g) were added into a series of glass stoppered flask containing 100 cm³ methylene blue solution (1000 ppm). These mixtures were kept at 30°C for 4 days. After 4 days, the concentrations of methylene blue were analyzed in a UV-Vis spectrophotometer (Shimadzu 1201). The amount adsorbed is calculated using the following equation:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

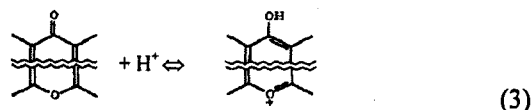
where q_e is the amount of methylene blue adsorbed per gram of adsorbent, V is the volume of liquid phase, C_o is the initial concentration of solution and C_e is the equilibrium concentration, and m is the amount of adsorbent.

4. Results and Discussion

In this work, the surface chemistry of activated carbon was treated with addition of acids. The changes of surface chemistry were determined by the surface basicity of the activated carbon. It was proposed by Leon y Leon *et al.* (1992) that the basicity of carbon surfaces arose from the combination of electron-donor acceptor and pyrone-type interactions. The protonation of basal plane sites on the carbon surfaces is shown by the following reaction:



where C_{π} was defined as a delocalized π electron on the graphitized carbon surface. The π electron may become localized as a result of the H_3O^+ addition where pyrone type structure (left hand side) that



consist of two non-neighboring oxygen atoms were postulated to constitute one basic site. These atoms were proposed to be preferably located in two different rings of a graphitic layer, to favor resonance stabilization of the positive charge.

These reactions would make the surface of carbon become positively charged and at the same time, it would adsorb oxygen anion from the solution to form surface oxides.

The results of Boehm titration on activated carbon with and without HNO₃ treatment are given in Figure 2. It can be seen that addition of HNO₃ increase significantly the equivalent of acidic surface oxides, i.e. carboxyl, lactone and phenol groups. It is clear that HNO₃ is a strong oxidant acid so it would oxidize carbon atoms and would make the carbon surfaces lose its electrons and become positively charged. Simultaneously, oxygen anions exist in the solution would be adsorbed to form surface oxides. The higher concentration of HNO₃ added the more positive its surface and many oxygen anions would be bonded to the carbon surface.

Figure 2(c) shows that untreated carbon and carbon treated with HNO₃ did not contain phenol group, except on the concentration of 9 and 12 M at 80°C. Because the higher concentration of HNO₃, the carbon surfaces became more positively charged and would adsorb hydroxyl anions from the solution to form phenol group. The formation of phenol at 80°C shows that at this temperature, activation energy of the formation of phenol group has been reached. However, in the same time, the formation of lactone group also occurs. At low acid concentration, the phenol group was not present on the carbon surface, the phenol group increase significantly with the increase of nitric acid concentration. However, the increase of phenol group will decrease of lactone group as shown in Figure 2(b) and (c), since the competition for the formation of these groups occurred as described earlier.

The decrease of phenol group at higher concentration of HNO₃ (12 M) is depicted in Figure 2(c). However, lactone group increase as shown in Figure 2(b). As the concentration of HNO₃ increased, the equivalent of acidic surface groups also increased, thus the probability of finding some carboxyl group close to phenol group increased as well.

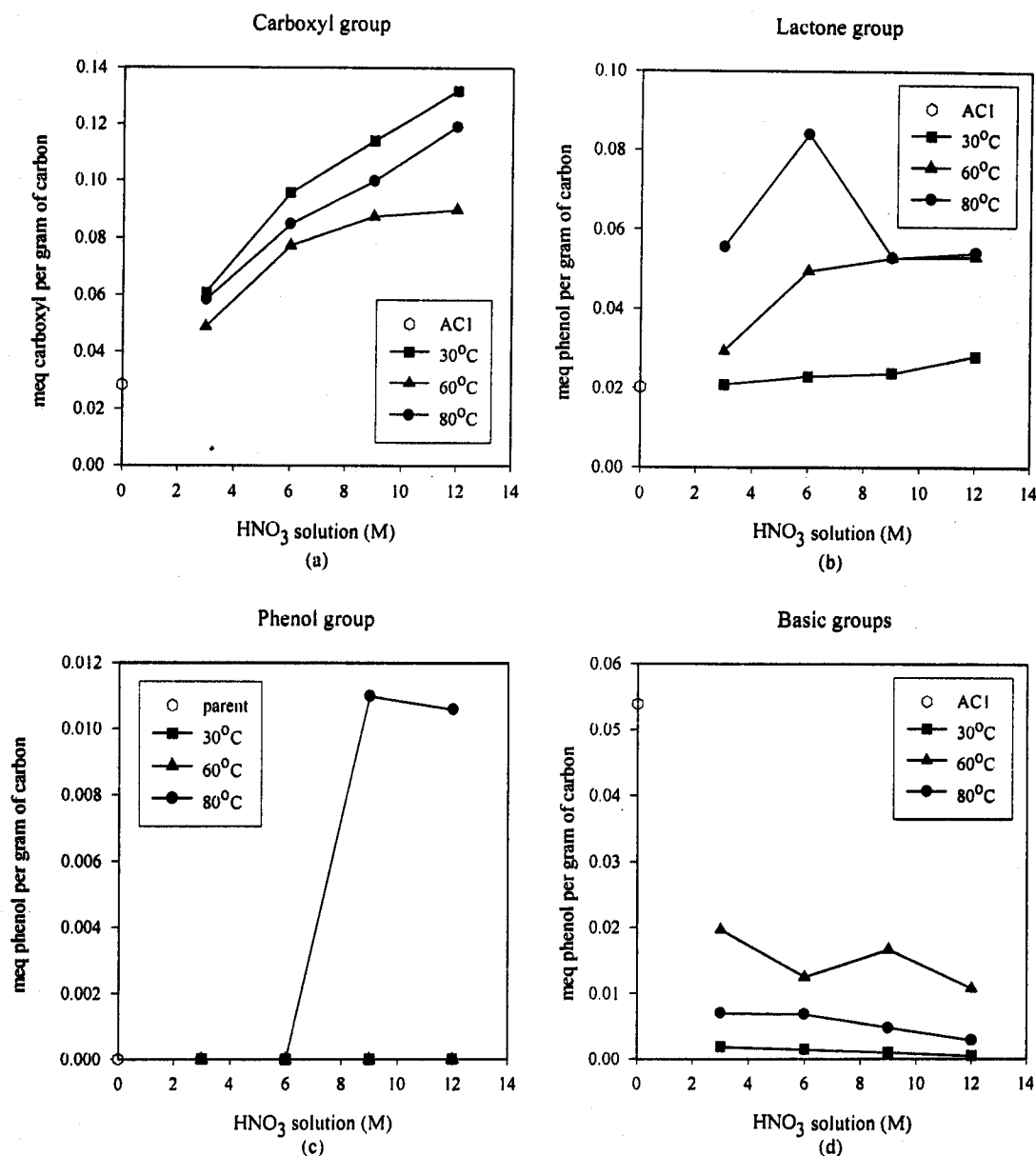
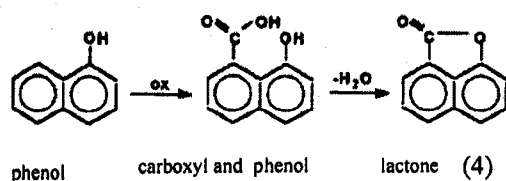


Figure 2. Equivalent of Acidic Surface Oxides (a-c) and Basic Groups (d) Resulted from Boehm Titration on Activated Carbons With and Without HNO₃ Treatment

Therefore, the formation of lactone group as shown by the sequence below is favored and the dehydration step would be occurred in the acid medium where the oxidation reaction is carried out.



The equivalent of the carboxyl group should decrease with the increase of the reactions between carboxyl and phenol groups (see eq. (4)). However, Figure 2(a) shows that carboxyl group did not decrease at all. It means that carbons modified by HNO₃, contain much carboxyl and not all of this group could be detected by Boehm titration. Therefore, the quantity of carboxyl reacted with phenol did not affect the equivalent of carboxyl group calculated from Boehm titration. Moreover, Figueiredo *et al.* (1999) have reported

that Boehm titration method fails to account total oxygen content of carbon materials if the materials have significant amount of oxygen content.

The influences of temperatures on the formation of acidic surface groups are shown in Figure 2(a) as well. Carboxyl group was formed most at 30°C. It means that at this temperature the activation energy of the formation of carboxyl

group has been reached. Thereby the higher temperature the more carboxyl group should have been formed. However, at 80°C the equivalent of carboxyl group is less than that obtained at 30°C. This is caused by the tendencies of carbon to form lactone group, because the activation energy for lactone formation was achieved at 80°C.

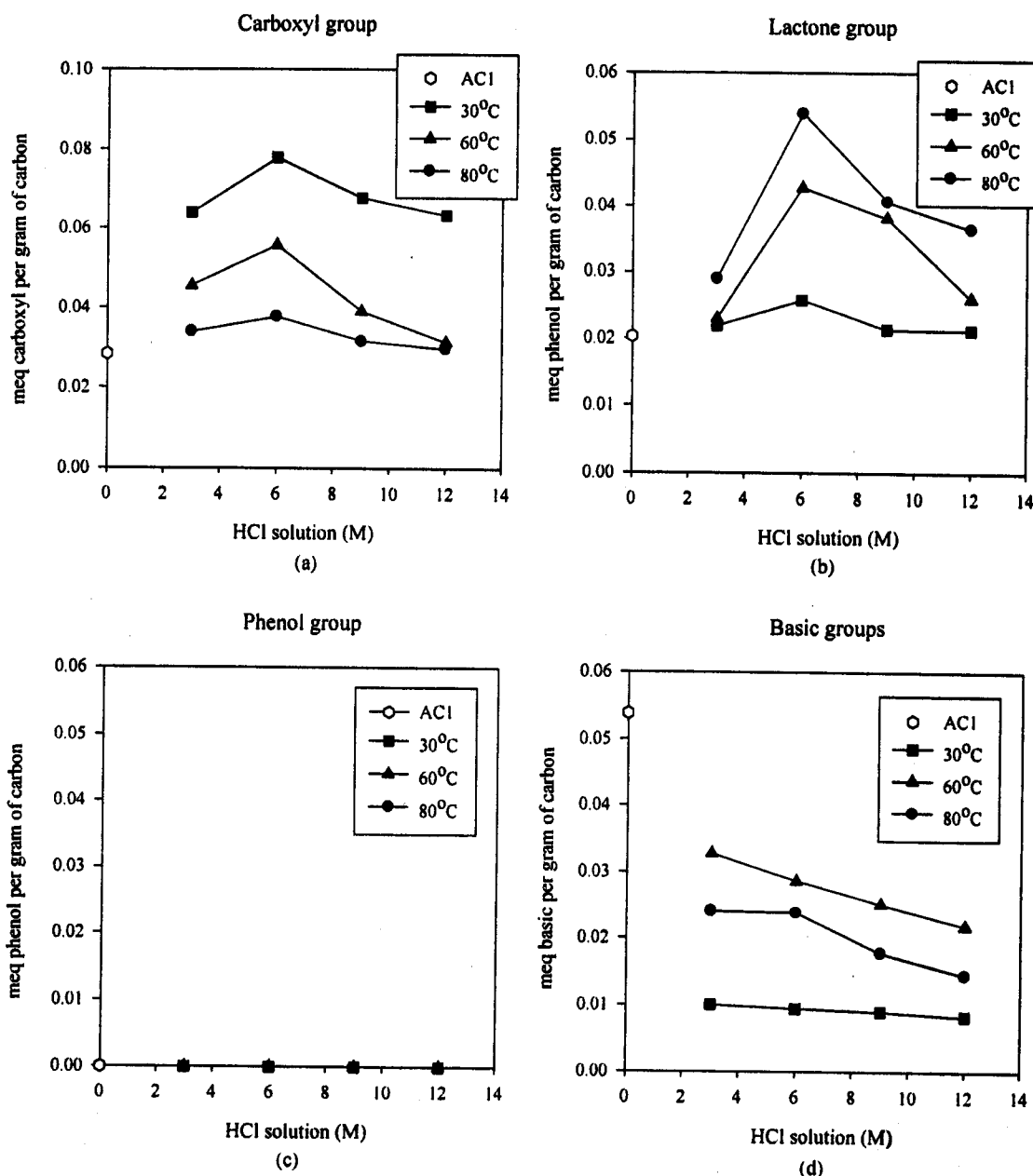


Figure 3. Equivalent of Acidic Surface Oxides (a-c) and Basic Groups (d) resulted from Boehm Titration on Activated Carbons With and Without HCl Treatment

From the result of Boehm titration presented in Figure 3, the equivalent of acidic surface oxides on the modified carbons by HCl are less than that obtained from HNO_3 treatment. It is obvious that HCl is non oxidant acid. Therefore, oxygen anion which reacted on the carbon surface was only come from the solvent (water).

As depicted in Figure 3(a-b), at low concentration of HCl (3 and 6 M), the treatment with HCl increased either carboxyl or lactone groups. While at higher concentration (9 and 12 M), carboxyl and lactone are slightly decrease due to the competition between oxygen and chlorine adsorbed on the carbon surface. At low concentration, oxygen anions present in the solution are higher than chloride ion. Therefore the chemical potential of oxygen for the adsorption into the pore of carbons was higher than chloride ion adsorption. On the contrary, at high concentration, chlorine was more dominant in the solution therefore the adsorption of Cl^- was favoured. Consequently, the equivalent of acidic surface oxides is decrease at high concentration of HCl.

Treatment with HCl does not change the equivalent of phenol group as shown in Figure 3(c). It indicates that carbon material used in this study contains a few of oxygen so the addition of acid did not affect significantly to the formation of phenol group. From this result, it can be concluded that the basicity of AC1 is mainly due to the delocalized π electrons.

The influences of temperatures to the equivalent of acidic groups can also be seen at Figure 3. This result is consistent with the result obtained by HNO_3 treated samples, the highest equivalent of carboxyl and lactone groups were achieved at 30° and 80°C , respectively. Since the formation of carboxyl is exothermic, equivalent of carboxyl decreased with increased in temperatures.

With the addition of acid solution, the reaction between acid and basic groups on activated carbons occurs. Therefore the equivalent of basic groups on carbons after treatment is less than untreated one. The higher concentration of acid added the more basic groups reacted with the acid leading to the decrease of the equivalent of basic groups. In contrast, at the concentration of HNO_3 9 M the equivalent of basic groups is still high. This might be caused by the impurities covered on the carbon surfaces, such as inorganic compounds. These impurities can hinder the protons' bonding on the carbon surface. As a result, it minimized the equivalent of basic groups that reacted with the acid.

Several factors play important roles in the adsorption of cations or anions exist in the solution by activated carbon. Radovic *et al.* (1997) have studied that the point of zero charge (pH_{PZC}) has been shown to be the important features of the surface chemistry of activated carbon. Many chemical and physical phenomena are associated with their pH_{PZC} value. Anions adsorption, for example, depends on the pH of the solution. Several studies indicated that when the pH value of a solution was lower than the pH_{PZC} of carbon, protonation on the carbon basal planes may occur at Lewis base site on the form of $\text{C}\pi\text{-H}_2\text{O}^+$ (Leon *et al.*, 1992). These protonated Lewis base site on carbon surfaces then adsorb anions in the solution. On the other hand, when pH of solution was higher than pH_{PZC} of carbon, the majority of the carboxylic surface oxygen groups will exist in the dissociated carboxylate form (COO^-) (Franz *et al.*, 2000). This will enhance cation adsorption. Thus, it is important to consider such phenomena on carbon surfaces and therefore determination of pH_{PZC} is also carried out in our study.

In this research, NaCl was used in the determination of pH_{PZC} . The use of NaCl as supporting electrolyte is to provide relatively constant ionic strength and activity coefficients for the carbon's slurries in order to facilitate the analysis of the data; in doing so, it also enhances ionic interaction between HCl/NaOH added and the surface basicity/acidity on carbon.

Five samples of activated carbon before and after treatment listed in Table 1 have been chosen as adsorbent for the adsorption of methylene blue and therefore the pH_{PZC} of these samples were also determined. These samples were chosen because of the extreme result of Boehm titration depicted in Figures 2 and 3.

Table 1. Activated Carbons Used in the Adsorption of Methylene Blue

Sample	Treatment
AC1	None
AC2	Oxidation with HNO_3 9 M at 60°C
AC3	Oxidation with HNO_3 9 M at 80°C
AC4	Treatment with HCl 6 M at 80°C
AC5	Treatment with HCl 12 M at 80°C

The result of pH_{PZC} on the five samples of carbons is presented in Figure 4. It is shown that modified carbon with acid can lower its pH_{PZC} value. As can be seen the values of pH_{PZC} are as follow: $\text{AC1} > \text{AC4} > \text{AC2} > \text{AC3} > \text{AC5}$. AC1 has high pH_{PZC} ; this was confirmed with that obtained from Boehm titration depicted in Figure 2. Higher equivalent of basic groups on AC1 are seen as

a result of high pH_{pzc} . Acid treatments can increase the surface acidity of activated carbons thus lowering its pH_{pzc} value. However, AC5 has the lowest pH_{pzc} . This contrast with the result obtained from Boehm titration. As can be seen in Figure 3, the acidic surface oxides of AC5 are decrease in the increase of HCl concentration. It means that the acidity of AC5 is not caused by the surface oxides but due to some Cl^- chemisorbed on the carbon surface. The existence of these atoms cannot be detected through Boehm titration method.

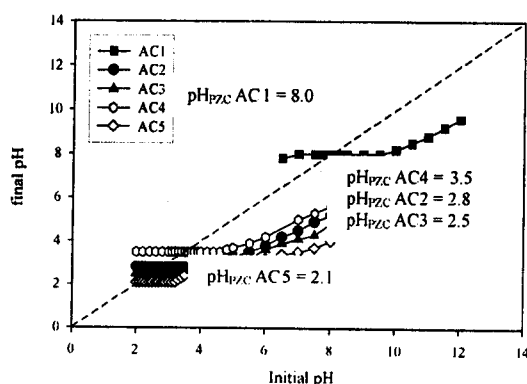


Figure 4. pH_{pzc} of Five Samples Obtained from pH Drift Method

Methylene blue (MB) is classified as basic dye. When dissolved in water, basic dyes have a cationic character. In the present work, the initial pH of the aqueous MB is about 7.6.

As mentioned before, activated carbons are materials with amphoteric character; thus, depending on the pH of the solution, their surfaces might be positively or negatively charged. A strong correlation between acidity/basicity and maximum adsorption capacity for MB are clearly shown in Figure 5.

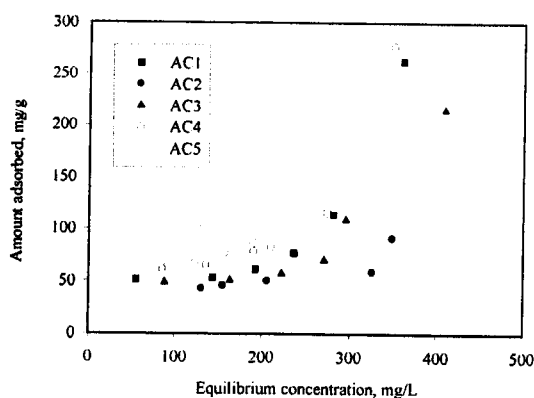


Figure 5. The Adsorption of Methylene Blue on Untreated and Chemically Modified AC1

AC2 and AC3 have $pH_{pzc} < pH$, thus MB^+ and the carbon surface carry opposite charges so this electrical change can lead to the enhancement of MB adsorption. In fact, when comparing to the untreated carbon, we observed that AC1, which has $pH_{pzc} > pH$ still exhibit a better performance for the adsorption of MB. It means there is another mechanism that can explain this phenomenon. It is evident that AC1 have high content of electron rich sites on their basal plane. The interaction of the molecules of MB and the activated carbon surface is expected to occur between the delocalized π electrons of the oxygen free Lewis basic sites and the free electrons of the dye molecule present in the aromatic rings and multiple bonds ($-N=C-$). The structure molecule of MB is depicted in Figure 6.

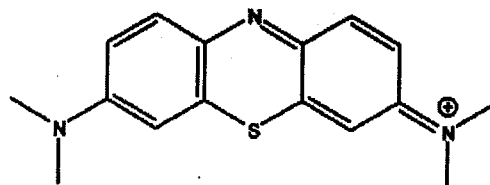


Figure 6. Molecular Structure of Methylene Blue

The lower adsorption capacity of AC2 and AC3 can be attributed to the fact that π electrons on the carbon aromatic sheets become localized because of the HNO_3 addition, and at the same time they can cause steric hindrance to the diffusion of MB molecules.

Nonetheless, Radovic *et al.* (1997) have reported the existence of two parallel adsorption mechanisms in the adsorption of organic molecules in activated carbons: one involving electrostatic interaction and a second one involving $\pi-\pi$ (dispersive) interaction. Thus, one cannot only account for the role of electrostatic interactions.

Carbons treated with HCl show the best performance for the adsorption of MB as can be seen in Figure 5. This was expected since AC4 and AC5 have $pH_{pzc} < pH$, thus electrostatic interactions occurred between MB^+ and the negatively carbon surface charge. AC5 has the highest adsorption capacity compared to AC4. It is clear that since $pH_{pzc} AC5 < pH_{pzc} AC4$, carbon surface of AC5 is pronounced to be more negatively charged than AC4 thus higher adsorption capacity is seen as a result of greater affinity of AC5 to MB molecules.

Comparing HNO_3 and HCl treated samples, from Figure 5, it can be seen that carbons treated by HCl show the highest adsorption capacity of MB. There are two main reasons in

explaining this behavior. First, according to the results of Boehm titrations depicted in Figure 2 and 3, HNO_3 treated samples have higher amounts of oxygen-containing surface groups. These abundant oxygen groups are complex: two carboxyl groups might give carboxylic anhydrides if they are close together; in close neighborhood to hydroxyl groups or carboxyl groups, carbonyl groups might condense to lactone groups or form lactols (Boehm, 1994). The presence of surface oxygen complexes may give high resistance for MB molecules to diffuse in the carbon pores. In the process of diffusion, pore blockage may occur due to the cross sectional of the pores being too small for the adsorbate to penetrate. Another key consideration is the polarity of the carbon surface. Treatment of activated carbon with HCl left some chlorine chemisorbed on its surface. The polarity of C-Cl on the carbon surface is higher than C-O, thus carbon treated with HCl gave greater Van der Waals interaction to the MB, which has polar nature as well.

The pore structure characteristics of the resulting carbons were determined by argon adsorption at 87.29 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. Prior to gas adsorption measurements, the carbon was degassed at 300°C in a vacuum condition for a period of at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_0) range from approximately 10^{-5} to 0.995. The BET surface area of the activated carbons was determined by application of the Brunauer-Emmett-Teller (BET). Untreated carbon and carbon modified by HNO_3 and HCl 3 M at 30°C were used as samples. The result of Argon adsorption isotherm at 87.29 K is presented in Figure 7. All samples have resembled shape of the adsorption isotherm curves. The isotherms obtained belong to a combination of Type I and Type IV isotherms. According to the IUPAC classification, Type I isotherm represents the microporous solid whereas Type IV isotherm is largely associated with mesoporous structures.

All of the isotherms have two characteristic regions; at low pressure region ($P/P_0 < 0.2$) significant uptake of argon occurred. This means that argon molecules are adsorbed in the microporous structure. The adsorption in micropores was interpreted according to the pore filling mechanism (Do, 1998), thus result in highly adsorbed volume. While at higher relative pressure ($P/P_0 > 0.2$), very little gas adsorbed with increased relative pressure. This indicates the existence of Type IV isotherm. Characteristic features of the Type IV isotherm are its hysteresis loop, which is

associated with capillary condensation taking place on the mesopores structure and the limiting uptake over a range of high P/P_0 .

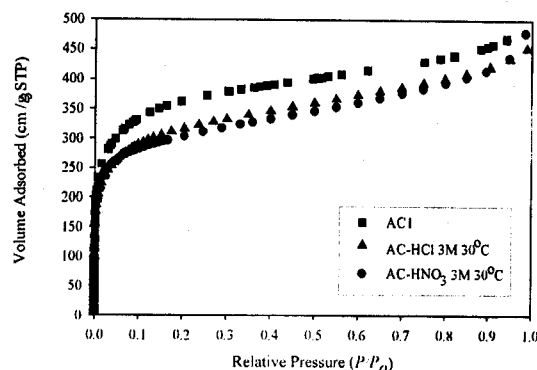


Figure 7. Argon Adsorption Isotherms of Untreated and Chemically Modified Acl

Carbon modified by HNO_3 shows significant increase at $P/P_0 > 0.9$. It is due the widening of micropores. Two mechanisms, acting at the same time, have been proposed to explain the breaking of the micropore walls (Moreno-Castilla *et al.*, 1998) after treatment with strong oxidant such as HNO_3 : one is by oxidation to produce oxygenated terminal groups, and the other is the mechanical destruction of the pores by the surface tension of the oxidizing solution. Introduction of a significant amount of oxygen containing groups to the carbon matrix contributed to the structural changes. To introduce those groups some carbon atoms from the walls have to be consumed causing wall destruction. Beside that, acidic treatment can remove some of the inorganic compounds on the carbon surface (Wang *et al.*, 1998). Therefore, the carbon microporosity is widening to the mesopores. At $0.2 < P/P_0 < 0.9$, this mesopore region is used as pores entrance to fill the micropore. After micropore volume filling, the adsorption amount keeps increasing with increasing relative pressure. Argon molecules began to adhere on mesopore walls and the adsorption amount undergoes a steep increase indicating capillary condensation at a pressure approaching the saturation.

The measured relative pressure and adsorbed volume of argon gas are commonly used in BET mathematical model to calculate the monolayer coverage of argon adsorbed on the adsorbent surfaces. The BET surface areas of all samples are given in Table 2. As can be seen, the BET surface areas are slightly decreased by the chemical modification thus result in low adsorption capacity of argon. It is due to the

blocking of the narrow pores by the surface functional groups introduced after treatment. For modified carbons, HCl treated sample has higher BET surface area. According to the result of Boehm titration presented in Figures 2 and 3, carbons treated by HNO₃ have high degree of surface oxygen complexes, therefore they can cause diffusional blockage of argon molecules to the interior carbon pores.

Tabel 2. BET Surface Area by Argon Isotherms

Sampel	S_{BET} (m ² /g)
ACI	1006
AC-HCl 3M 30°C	993
AC-HNO ₃ 3 M 30°C	972

5. Conclusions

From the result of the present work, it can be concluded that: (1) both treatment with oxidant (HNO₃) and non-oxidant acid (HCl) at different temperatures and concentrations can increase the surface acidity and decrease its basicity, (2) treatment with HCl yield activated carbon with high adsorption capacity of methylene blue compared to the untreated one, (3) in contrast, treatment with HNO₃ gave the worst performance to the methylene blue removal.

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