
ADSORPTION OF SEVERAL ACID DYES FROM AQUEOUS SOLUTION USING ACTIVATED CARBON DERIVED FROM TEAK SAWDUST: EFFECT OF SURFACE ACIDITY

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Abstract

The adsorption of acid blue 9, acid blue 74 and acid orange 51 from aqueous solution using activated carbon derived from teak sawdust was studied in terms of dye molecular size, pore size and surface acidity of activated carbon. The experimental adsorption data were correlated with Langmuir equation. It was found that Langmuir equation could describe the adsorption data well with R^2 higher than 0.95. The surface acidity of activated carbon plays a key role in dye adsorption on modified activated carbon. The interaction between the oxygen-free Lewis basic sites and the free electrons of the dye molecule were the main adsorption mechanism in the adsorption process on modified activated carbon. The adsorption capacities of activated carbon on the adsorption of acid dyes decreased in the order unmodified > modified at 100°C > modified at 150°C

Keywords : Activated Carbon, Adsorption, Pore Size, Surface Acidity

Abstrak

Adsorpsi zat warna acid blue 9, acid blue 74, dan acid orange 51 dari larutan dengan menggunakan karbon aktif yang terbuat dari serbuk gergaji kayu jati dipelajari sebagai fungsi ukuran molekul zat warna, ukuran pori dan sifat asam permukaan karbon aktif. Data percobaan adsorpsi kemudian dikorelasikan dengan menggunakan persamaan Langmuir. Dari hasil percobaan yang diperoleh dapat dilihat bahwa persamaan Langmuir dapat menggambarkan data adsorpsi isotermal dengan baik dengan R^2 lebih besar dari 0,95. Sifat asam permukaan memegang peranan yang sangat penting pada proses adsorpsi zat warna pada karbon aktif yang telah dimodifikasi. Interaksi antara bagian oxygen-free Lewis yang bersifat basa dan elektron elektron bebas dari molekul zat warna merupakan mekanisme adsorpsi utama pada proses adsorpsi dengan menggunakan karbon aktif yang telah dimodifikasi. Kemampuan adsorpsi karbon aktif terhadap zat warna yang bersifat asam menurun dengan tingkatan karbon aktif tidak dimodifikasi > modifikasi pada 100°C > modifikasi pada 150°C.

Kata kunci : Adsorpsi, Karbon Aktif, Sifat Asam Permukaan, Ukuran Pori

1. Introduction

Synthetic dyes are extensively used in many industries such as textile, paper, ceramics, cosmetic industries, etc. The direct discharge of colored wastewater from these kinds of industries to water streams can damage the environment because even at low concentration of dyes will reduce the transmission of sunlight into streams and therefore reduces photosynthetic action. Wide range of methods have been developed for handling water or wastewater contain synthetic dyes, and the most extensively used method is adsorption process (Acemioglu, 2004; Mohammed, 2004; Malik, 2004; Martin et al., 2003; Nakagawa., 2004; Papic et al., 2004; Wang et al., 2005). Activated carbon is currently the most widely used adsorbent for this purpose (Malik 2004; Martin et al, 2003; Mohammed, 2004; Nakagawa et al., 2004).

Activated carbons are materials having complex porous structures with associated energetic as well chemical inhomogeneities. Their structural heterogeneity is a result of the existence of micropores, mesopores, and macropores of different sizes and shapes. The presence of micropores in these solids substantially increases their sorption capacities over those for nonporous and mesoporous materials. The macropores and large mesopores play an important role in the molecular transport process, whereas the remaining smaller pores determine the sorption property of a given carbon (Ismadji and Bhatia, 2000). The energetic and chemical heterogeneities are determined by the variety of surface functional groups, irregularities, and strongly bound impurities, as well as structural nonuniformity. This heterogeneity considerably influences the process of physical adsorption (Ismadji and Bhatia, 2000b, 2002).

Adsorption in the liquid phase is in general a more complex phenomenon than in gas-phase adsorption. In liquid phase adsorption, the adsorbed molecules are not necessarily tightly packed with identical orientation. The presence of solvent molecules, surface acidity of carbon, and the formation of micelles from adsorbed molecules also increases the complexity of liquid phase adsorption (Ismadji and Bhatia, 2000a). Adsorption from the liquid phase is also influenced by many factors, such as pH, solubility of the adsorbate in the solvent, and temperature as well adsorptive concentration.

The main objectives of the present work were to study the effect of sulfuric acid treatment of activated carbon prepared from teak sawdust on liquid phase adsorption of acid blue 9, acid blue 74, and acid orange 51. The adsorption isotherm of

these acid dyes on activated carbon derived from teak sawdust was analyzed by Langmuir model to determine the adsorption capacity of each dye.

2. Fundamental

Microporous carbons, and in particular activated carbons, are well known for their high sorptive capacities. Activated carbon is widely used for adsorption of organic chemicals in wastewater treatment and drinking water. Both powdered and granular activated carbons are employed, and the quality of activated carbons is typically assessed by the iodine number or the BET surface area obtained from nitrogen adsorption at 77 K. However, the carbon usage rate and thus the cost of activated carbon adsorption processes is frequently unrelated to these parameters because the molecular dimensions and chemical characteristics of iodine and nitrogen are not representative of typical organic contaminants in aqueous solution. Consequently, these parameters do not recognize the importance of molecular sieving, i.e., the exclusion of larger organic contaminants from adsorbent pores that are accessible to nitrogen or iodine. Furthermore, effects of pore surface chemistry on adsorbate/adsorbent and solvent/adsorbent interactions are not accounted for.

Activated carbons can be produced from a variety of carbonaceous materials, including wood, coal, lignin, coconut shells, and sugar. Its unique adsorption properties result from its high-surface area, micropores, and broad range of surface functional groups. The structure of activated carbon comprises of carbon atoms that are ordered in parallel stacks of hexagonal layers, extensively cross-linked and tetrahedrally bonded. Several heteroatoms, including oxygen, hydrogen, nitrogen, and others, can be found in the carbon matrix, in the form of single atoms and/or functional groups. They are chemically connected to the carbon atoms with unsaturated valences that are located at the edges of graphite basal planes (Karanfil and Kilduff, 1999).

Oxygen is the dominant heteroatom in the carbon matrix, and the presence of functional groups, such as carboxyl, carbonyl, phenols, enols, lactones, and quinones, has been postulated. Surface functional groups influence adsorption properties and reactivities of activated carbons. Several techniques, including heat treatment, oxidation, amination, and impregnation with various inorganic compounds, are available to modify activated carbons. These modifications may change surface reactivity as well as structural and chemical properties of the carbon (Karanfil and Kilduff, 1999).

Activated carbons assume an acidic character when exposed to oxygen between 200 and 700°C or to oxidants such as hydrogen peroxide, nitric acid, or nitric and sulfuric acid mixtures in aqueous solution. The increased acidity is primarily explained by the formation of carboxylic acid and phenolic hydroxyl groups. The oxidation also increased the surface concentration of quinone carbonyl groups (Li et al., 2002)

The presence of basic oxygen-containing functionalities such as chromene- and pyrone-type structures has also been postulated. However, a consensus is developing that the basic character of activated carbons arises primarily from delocalized π -electrons on the condensed polyaromatic sheets. These electron-rich Lewis base sites develop as oxygen is removed from the activated carbon surface, e.g. by heat treatment in an inert atmosphere.

This treatment not only removes inherently acidic groups, but also other oxygen-containing functionalities that decrease the basicity of activated carbons by attracting and thus localizing π -electrons of the condensed, polyaromatic sheets. The removal of oxygen not only renders an activated carbon surface more basic but also less polar, a desirable trait when the adsorption of organic contaminants from aqueous solution is the primary objective. While heat treatment in an inert atmosphere effectively removes oxygen-containing functional groups from the activated carbon surface, it produces highly reactive sites such as free-radical edge sites and dangling carbon atoms. As a result, re-exposure of such carbons to the atmosphere results in oxygen adsorption and the consequent loss of basic and hydrophobic properties (Li et al., 2002)

The surface oxides on a carbon can have acidic as well as basic properties and can be conveniently determined by titration methods. The functional groups or surface oxides in the activated carbon differ in their acidities and can be differentiated by neutralization with 0.05 N solutions of NaHCO_3 , Na_2CO_3 and NaOH , respectively (Boehm, 2002).

The acidity of a given functional group depends on its chemical environment, i.e., the size and shape of the polyaromatic layers, the presence and position of other substituents, and the charge of neighboring dissociated groups. However, the differences in acidity of the various types of functional groups seem to be sufficiently large to allow differentiation by the simple titration method, e.g., the difference between NaOH and Na_2CO_3 consumption corresponds to the weakly acidic phenolic groups.

3. Experimental

About 500 grams of teak sawdust were placed in the pyrolysis reactor with vacuum condition (total pressure around 20 kPa) then heated to a temperature of 600°C with the heating rate of 20°C/min and held at this temperature for 1 hour. Then the resulting char was allowed to cool under the same vacuum condition. The steam activation of the resulting char was carried out at the temperature of 850°C in a vertical tube reactor. The char was placed in a reactor, and then this reactor was purged with 150 mL/min of nitrogen for at least 1 h. Under the same nitrogen flow, this char was heated to a desired activation temperature. When the temperature was reached, the nitrogen flow was switched to steam (100% H_2O , 0.02 g/min) and held for 5 h. After 5 hours, the resulting carbon was then cooled to room temperature in an inert atmosphere, and stored in the desiccator, if not used directly. Schematic diagram of the equipment used for the activated carbon preparation is shown in Figure 1.

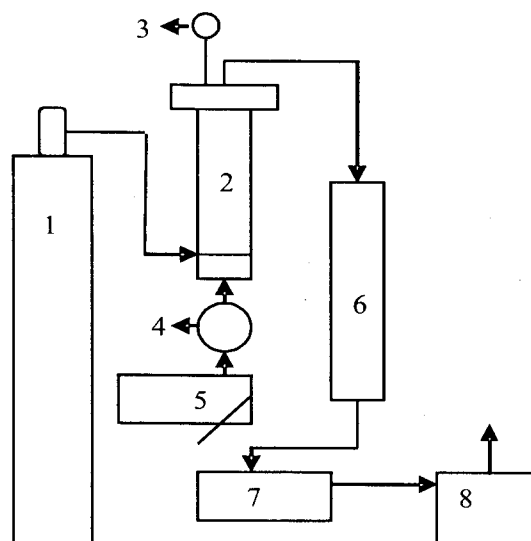


Figure 1. Schematic diagram of pyrolysis reactor (1. Nitrogen bottle, 2. Reactor, 3. Manometer, 4. Preheater, 5. Steam generator, 6. Condensing system, 7. Tar collector and 8. Vacuum pump)

Surface chemistry modification of the carbon with concentrated sulfuric acid (96%) was performed using a flask fitted with a water reflux condenser apparatus at two different temperatures (100°C and 150°C). Initially, a known amount of concentrated sulfuric acid was introduced into 250 cm^3 of round bottom flask containing about 30 grams of activated carbon. The flask then

connected to the water reflux condenser and heated at the desired temperature for 3 hours. After the modification treatment, the carbon was washed with distilled water until the filtrate water was free of sulfate (tested with BaCl_2). Finally it was dried in vacuum drying oven at 110°C for 24 h and stored in desiccator.

Surface acidity (phenol, lactone, and carboxyl groups) of the activated carbon was determined by using the classical Boehm's method (Jiang et al., 2003). A known amount of activated carbon (0.5 g) was added to 25 mL 0.05 N of standard base (NaOH , Na_2CO_3 , and NaHCO_3) solutions and then held for 24 h. The acidic surface oxides were determined by back-titration with standard HCl aqueous solution after reaching the equilibrium. Here, sodium bicarbonate (NaHCO_3) only neutralized the carboxylic groups, while sodium carbonate (Na_2CO_3) neutralized lactone and carboxyl groups, and weakly acidic phenolic groups were neutralized by sodium hydroxide (NaOH) (Jiang et al., 2003).

The pore structure characteristics of the activated carbons were determined by nitrogen adsorption at 77.35 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. The BET surface area, micropore volume and micropore surface area of the activated carbons were determined by application of the Brunauer-Emmett-Teller (BET) and Dubinin-Astakhov (DA) analysis software available with the instrument, respectively. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The pore size distribution of carbon was determined from argon adsorption isotherm data using the Micromeritics density functional theory (DFT) software, with medium regularization. The argon adsorption experiment was carried out at 87.35 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer.

The dyes used in the adsorption experiments were acid blue 9, acid blue 74, and acid orange 51 and obtained as analytical grade. The dyes used in this study were obtained from Sigma Aldrich Co Singapore and used without any

further treatment. The physical information and molecular structure about these dyes are given in Table 1 and Figure 1, respectively.

In the adsorption experiments, the dyes solutions were prepared by mixing a known amount of dyes with double distilled water to yield various desired concentrations. The adsorption experiments were carried out isothermally in static mode at three different temperatures, 303.15 K, 313.15 K, and 323.15 K. The experiments were conducted by adding a fixed amount of activated carbon (0.1 to 1.0 g) to a series of 250 mL glass-stoppered flasks filled with 200 mL of diluted dyes solutions. The flasks were then placed in a thermostatic shaker bath (Mettmert Type WB-14 equipped with temperature controller SV-1422) and shaken at 120 rpm for 48 hours. The accuracy of the temperature controller is 0.1 K.

Product analysis showed that the equilibrium condition was reached after about 24 hours. The adsorption experiments were conducted without any control over the pH of the aqueous phase. The initial and equilibrium concentrations of all liquid samples were analyzed using UV-Vis Spectrophotometer Shimadzu UV-1201. The amount of dye adsorbed (q) on the activated carbon was determined as follows

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

where C_o and C_e are initial and equilibrium concentrations of dyes, respectively. V is the volume of the solution and m is the mass of activated carbon.

The adsorption of experimental data were well correlated with Langmuir model which is shown in equation (2), as follows:

$$q = \frac{Q_m K C_e}{1 + K C_e} \quad (2)$$

Where Q_m and K are Langmuir isotherm parameters constant. Parameter Q_m represents the adsorption capacity of the adsorbents while K is the affinity coefficient. The parameters Q_m and K were determined by non-linear least square method using Sigma Plot program.

Table 1. Properties of dyes used in this study

| Property | Acid blue 9 | Acid blue 74 | Acid orange 51 |
|-----------------------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------------|
| CAS | 2650-18-2 | 860-22-0 | 8003-88-1 |
| Molecular formula | $\text{C}_{37}\text{H}_{36}\text{N}_2\text{O}_9\text{S}_3 \cdot 2\text{NH}_4$ | $\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$ | $\text{C}_{36}\text{H}_{26}\text{N}_6\text{Na}_2\text{O}_{11}\text{S}_3$ |
| Certified dye content | 65 % | 85 % | 50 % |
| λ_{max} (nm) | 408 | 608 | 446 |

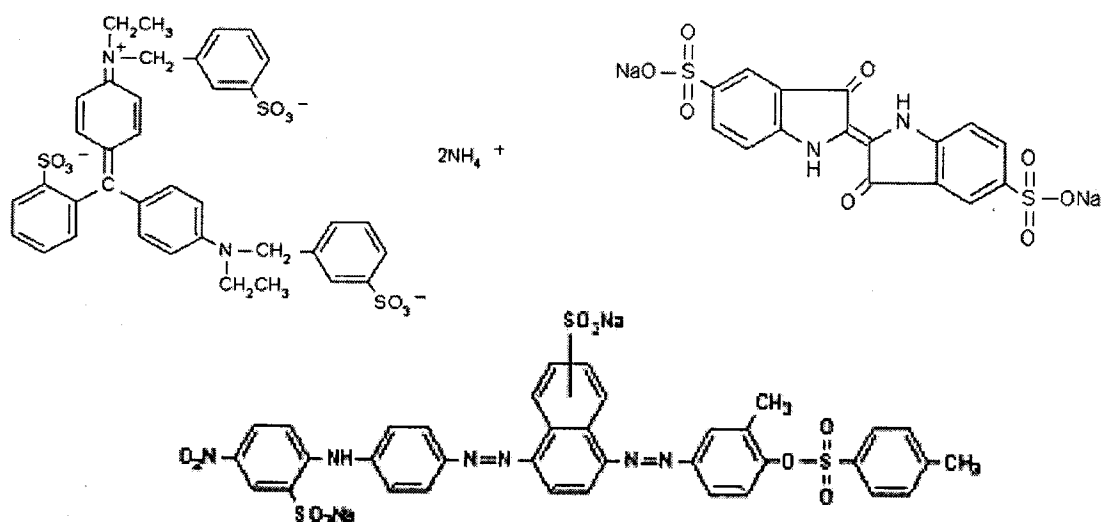


Figure 2. Molecular structure of (a) acid blue 9, (b) acid blue 74, and (c) acid orange 51

4. Results and Discussion

The pore characteristics of the activated carbon from teak sawdust were used in this study and its chemically modified are summarized in Table 2. While the nitrogen adsorption isotherms and DFT pore size distributions are given in Figures 3 and 4, respectively.

Table 2. Pore characteristic of activated carbon from teak sawdust

| Pore characteristic | Initial | Modified at 100°C | Modified at 150°C |
|-------------------------------------------|---------|-------------------|-------------------|
| BET Surface Area, m ² /g | 1150 | 1158 | 1189 |
| Micropore Surface Area, m ² /g | 1048 | 1049 | 1007 |
| Micropore Volume, cm ³ /g | 0.43 | 0.43 | 0.41 |

Table 2 shows that the activated carbon modified with sulfuric acid at 100°C and 150°C gave insignificantly change of the carbon pore structures.

The adsorption isotherm of activated carbon from teak sawdust and its modification as seen in Figure 3 clearly shows the largely microporous nature of the carbon, with some mesopores leading to gradual increase in adsorption after the initial filling of the micropores, followed by more rapid increase near saturation. It can be seen in Figure 3 that the oxidation with sulfuric acid did not change the shape of nitrogen adsorption isotherm. This phenomenon indicates that the treatment with sulfuric acid did not damage the pore structure of carbon. This result is in good agreement with the pore size distribution as describe below.

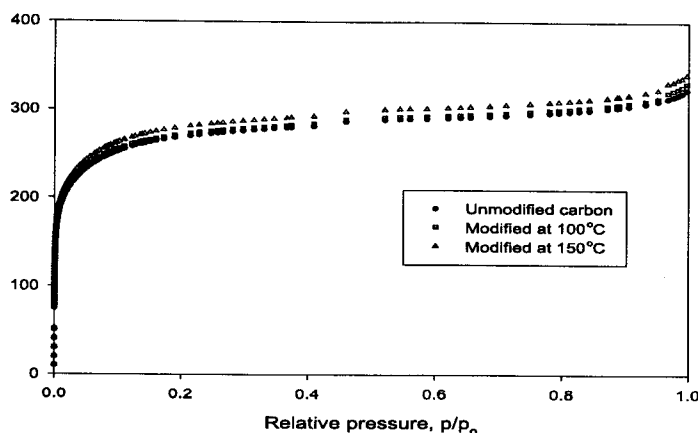


Figure 3. Nitrogen adsorption isotherm on activated carbon from teak sawdust (in cm³/g STP)

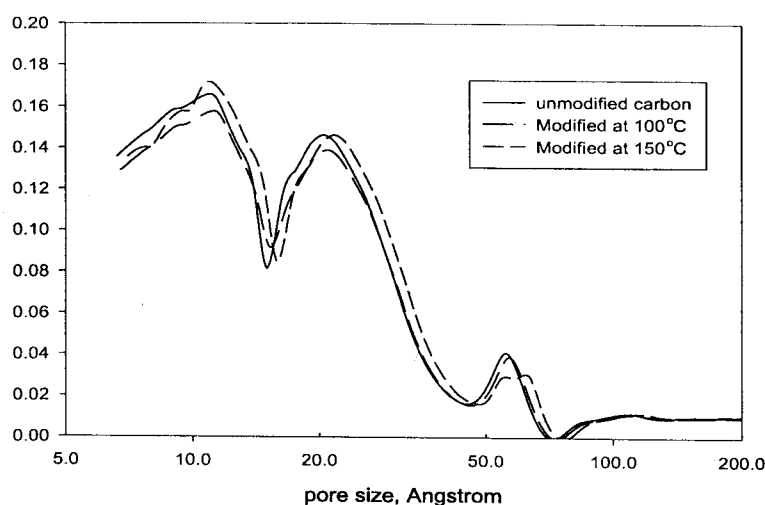


Figure 4. The pore size distribution of activated carbon from teak sawdust $f(H)$, cm^3/gA

The structural heterogeneity of porous material is generally characterized in terms of the pore size distribution. This pore size distribution represent a model of solid internal structure, which assumes that an equivalent set of non-interacting and regularly shaped model pores can represent the complex void spaces within the real solid. The pore size distribution is closely related to both kinetic and equilibrium properties of porous material, and perhaps is the most important aspect for characterizing the structural heterogeneity of porous materials used in industrial application. Here, the argon adsorption with DFT (density functional theory) analysis of the data is used to provide independent pore size distribution.

In this research the argon adsorption data were used instead of the nitrogen isotherm because when this method (DFT) applied to nitrogen isotherm suffer from the drawback that interactions of surface chemical heterogeneities with quadrupolar nitrogen can affect the pore size distribution determined. The interpretation of argon adsorption isotherm on the activated carbon was used in this study, by DFT model, showed that the carbon used in this study had microporous and mesoporous structure as indicated in Figure 4.

Table 3 shows the amount of acidic surface groups of unmodified and modified activated carbon. As mentioned before, sodium bicarbonate (NaHCO_3) only neutralized the carboxylic groups,

while sodium carbonate (Na_2CO_3) neutralized lactone and carboxyl groups, and weakly acidic phenolic groups were neutralized by sodium hydroxide (NaOH). It is clear that the treatment of carbon with concentrated sulfuric acid produces more acidic surface groups. The amount of phenolic, lactone and carboxyl groups increased with increasing the temperature (Table 3).

In the liquid phase adsorption, the molecular size of organic compounds also plays a very strong role. If the molecular size of organic compound is larger than adsorbent pore sizes, the available pores become un-accessible. In this study, the molecular size of each dye was estimated using a molecular structure simulation method, implemented in Cambridge SoftChem3D software package.

The molecular size calculations by the molecular structure simulation are based on geometry optimization of the potential energy surfaces of the molecule. In the geometry optimization, the atomic coordinates in the compound are systematically modified in the model to identify a local energy minimum. In the first step, the structural model of the molecules is created through the geometry optimization and then the model of the molecule is rotated in different angles and axis until the critical size of the molecule is found.

Table 3. Surface acidity of activated carbons by Boehm's method

| Sample | Surface acidity (meq/g) | | | Total |
|--------------------|-------------------------|---------|--------|--------|
| | carboxyl | Lactone | Phenol | |
| Unmodified | 0.0104 | 0.0254 | 0.0020 | 0.0378 |
| Modified at 100 °C | 0.2508 | 0.1831 | 0.1172 | 0.5511 |
| Modified at 150 °C | 0.4125 | 0.2982 | 0.1274 | 0.8381 |

Table 4. Molecular sizes of dyes obtained by molecular simulation

| Dye | Molecular weight | Molecular size, nm |
|----------------|------------------|--------------------|
| Acid blue 9 | 784 | 1.86 x 1.49 x 1.06 |
| Acid blue 74 | 466 | 1.55 x 0.64 x 0.41 |
| Acid orange 51 | 860 | 2.98 x 0.96 x 1.18 |

These processes are iterative and begin at some starting geometry and continue until convergence is achieved, at which point the minimization process terminates. The ability of this technique to converge to a minimum strongly depends on the starting geometry that we create, the potential energy function used, and the

convergence criteria (Ismadji and Bhatia, 2003). The critical molecular sizes of dyes used in this study were obtained by this molecular simulation are shown in Table 4. For the three dyes used in this study, the molecular size follows the order acid orange 5 > acid blue 9 > acid blue 74.

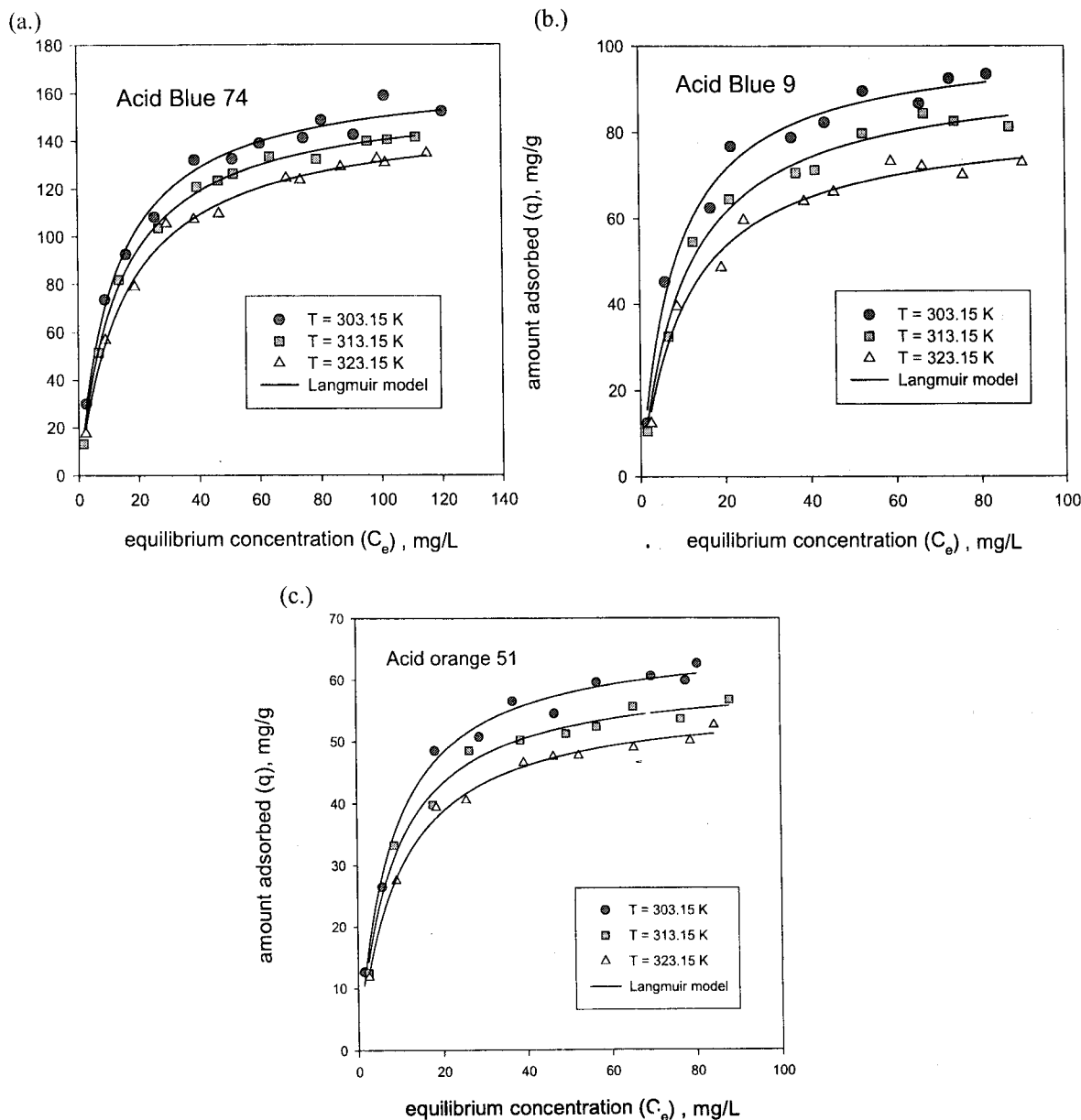


Figure 5. Adsorption of acid dyes (a: acid blue 9, b: acid blue 74, and c: acid orange 51) onto unmodified activated carbon

The adsorption isotherms of acid blue 9, acid blue 74, and acid orange 51 on unmodified activated carbon prepared from teak sawdust are given in Figure 5. In this figure, the experimental data are given in symbols, while the plots of data using original Langmuir model (eq.2) are given in solid lines. Figures 6 and 7 depict the adsorption

isotherms of acid blue 9, acid blue 74, and acid orange 51 on modified activated carbon at 100°C and 150°C, respectively. The Langmuir isotherm constants Q_m and K obtained by polynomial regression fit for solute-adsorbent combination are given in Table 5.

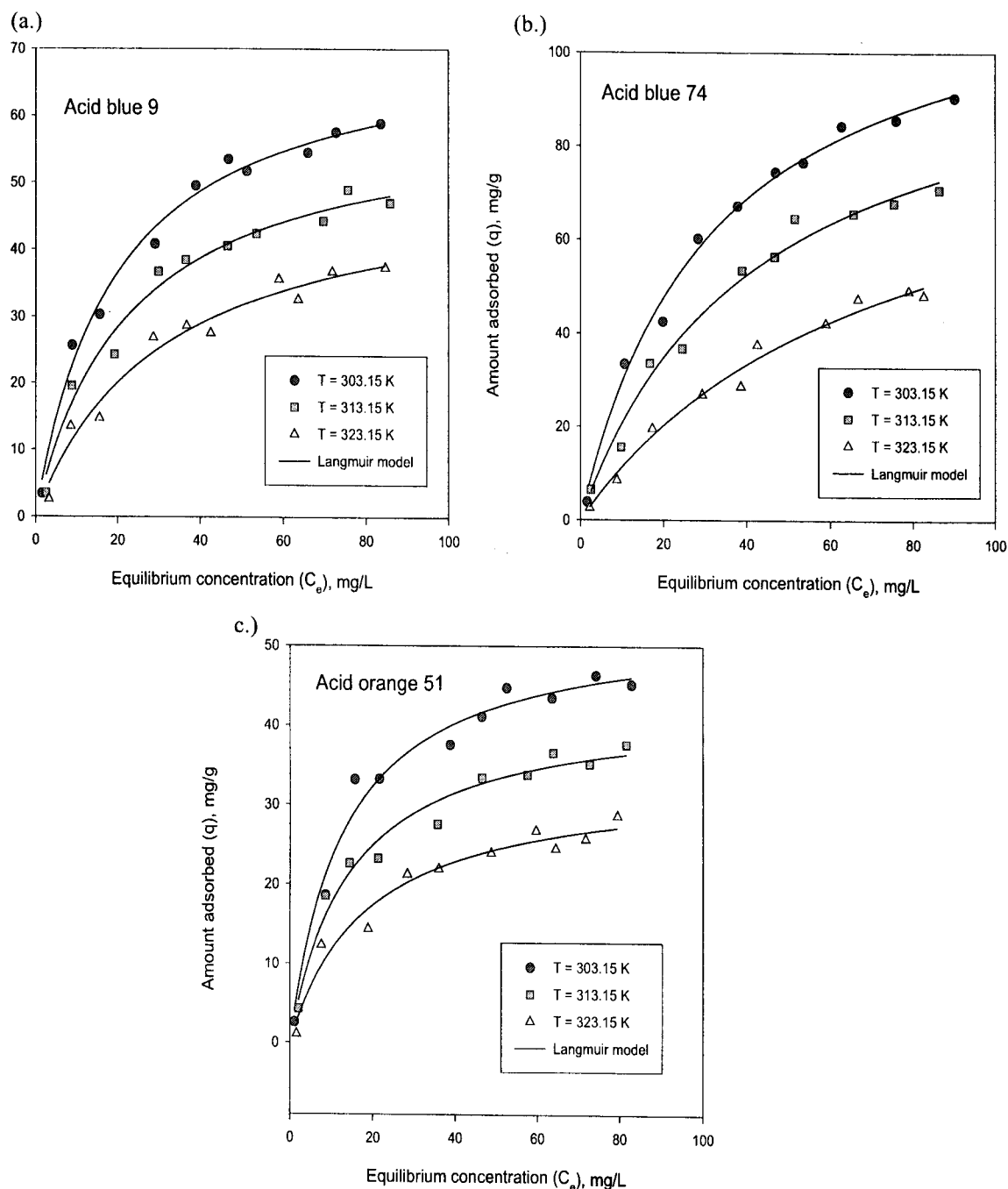


Figure 6. Adsorption isotherm of dyes (a: acid blue 9, b: acid blue 74, and c: acid orange 51) on modified activated

Table 5. Langmuir parameters constant for the adsorption of dyes on unmodified activated carbon derived from teak sawdust

| Activated carbon | Dye | Temperature, K | Q_m , mg/g | K , L/mg | R^2 |
|------------------|----------------|----------------|--------------|------------|-------|
| Unmodified | Acid Blue 9 | 303.15 | 101.22 | 0.1171 | 0.983 |
| | | 313.15 | 94.35 | 0.0916 | 0.986 |
| | | 323.15 | 83.19 | 0.0888 | 0.982 |
| | Acid Blue 74 | 303.15 | 168.35 | 0.0808 | 0.987 |
| | | 313.15 | 159.26 | 0.0734 | 0.998 |
| | | 323.15 | 152.03 | 0.0631 | 0.993 |
| | Acid Orange 51 | 303.15 | 66.99 | 0.1263 | 0.988 |
| | | 313.15 | 60.98 | 0.1213 | 0.986 |
| | | 323.15 | 57.04 | 0.1047 | 0.994 |

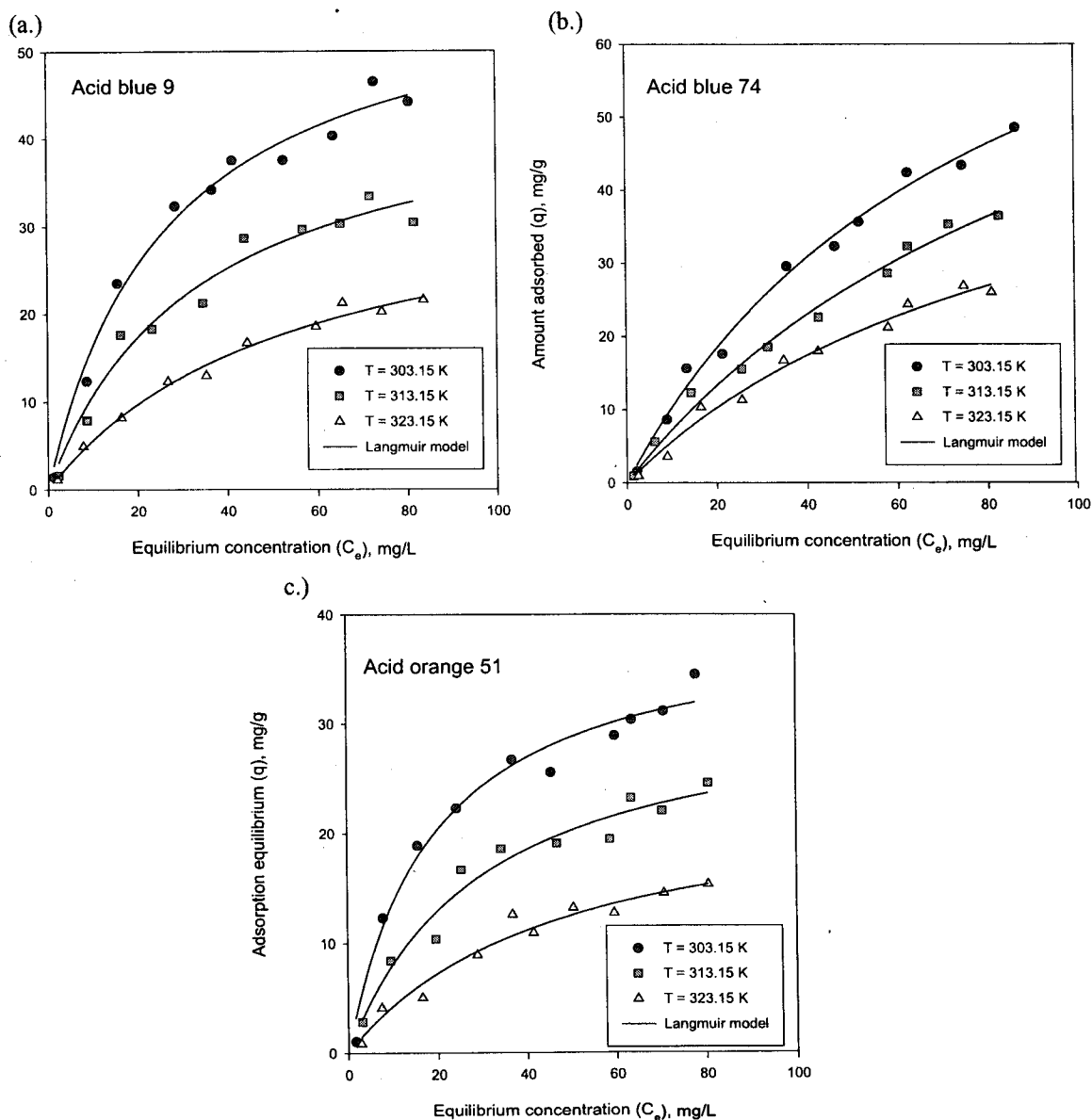


Figure 7. Adsorption isotherm of dyes (a: acid blue 9, b: acid blue 74, and c: acid orange 51) on modified activated carbon with concentrated sulfuric acid at 150°C

For unmodified activated carbon, it is clear that Langmuir equation can represent the adsorption equilibrium data very well (Figure 5). The adsorption capacity of the adsorbent strongly depends on the molecular size of the adsorbate as indicated in Table 5.

The activated carbon used in this study had two pore structures: microporous and mesoporous as indicated in Figure 4. For giant molecules acid orange 51, the adsorption only took place in mesopores since the molecular dimension of this dye exceeds over micropore size of the carbon. Since the activated carbon used in this study has micropores sizes ranging from 0.4 – 2 nm (Figure 3), it is clear that the micropores of the carbons cannot be fully accessed by acid blue 9 and acid blue 74 molecules as well. Table 5 reveals that the adsorption capacity (Q_m) of unmodified activated carbon follows the order acid blue 74 > acid blue 9 > acid orange 51.

The molecular weight of organic compounds also plays a very strong role in liquid phase adsorption. The molecular weight of the dyes used follows acid orange 51 > acid blue 9 > acid blue 74. With the increase in molecular weight the interaction forces between the solute and adsorbent also become stronger (Martin et al., 2003), leading to higher affinity coefficient, K , as seen in Table 5.

Temperature is well known to play an important role in adsorption in activated carbons, generally having a negative influence on the amount adsorbed. The adsorption of organic compounds is an exothermic process and the physical bonding between the organic molecules and the active sites of the carbon will weaken with increasing temperature. This behavior was also observed in our experiments as indicated in the adsorption data depicted in Figure 5.

Figures 6 and 7 depict the adsorption isotherm of dyes on modified activated carbon using concentrated sulfuric acid at 100°C and 150°C, respectively. While, the Langmuir parameters for both modified activated carbon are summarized in Tables 6 and 7.

For the three acid dyes studied, a similar behavior was observed, the adsorption capacity decrease with increasing the acidity of the material (Table 3). Since the pore structure of the carbon did not change with sulfuric acid modification as seen in Figures 3 and 4, here the pore structures of the activated carbons played a secondary role in terms of dye removal capacities. Therefore, the influence of pore structures of modified activated carbons on dye uptakes could not be entirely ruled out in this study. However, the activated carbons with similar surface acidity but with larger porosity would be more effective for acid dyes removal.

Table 6. Langmuir parameters constant for the adsorption of dyes on activated carbon derived from teak sawdust modified with sulfuric acid at 100°C

| Activated carbon | Dye | Temperature, K | Q_m , mg/g | K , L/mg | R^2 |
|-------------------|----------------|----------------|--------------|------------|-------|
| Modified at 100°C | Acid Blue 9 | 303.15 | 72.61 | 0.0508 | 0.988 |
| | | 313.15 | 60.87 | 0.0438 | 0.978 |
| | | 323.15 | 51.66 | 0.0318 | 0.971 |
| | Acid Blue 74 | 303.15 | 123.46 | 0.0313 | 0.992 |
| | | 313.15 | 108.11 | 0.0236 | 0.984 |
| | | 323.15 | 95.12 | 0.0135 | 0.984 |
| | Acid Orange 51 | 303.15 | 53.23 | 0.0772 | 0.979 |
| | | 313.15 | 42.65 | 0.0703 | 0.971 |
| | | 323.15 | 33.38 | 0.543 | 0.964 |

Table 7. Langmuir parameters constant for the adsorption of dyes on activated carbon derived from teak sawdust modified with sulfuric acid at 150°C

| Activated carbon | Dye | Temperature, K | Q_m , mg/g | K , L/mg | R^2 |
|-------------------|----------------|----------------|--------------|------------|-------|
| Modified at 150°C | Acid Blue 9 | 303.15 | 60.05 | 0.0370 | 0.984 |
| | | 313.15 | 46.35 | 0.0298 | 0.968 |
| | | 323.15 | 36.14 | 0.0183 | 0.989 |
| | Acid Blue 74 | 303.15 | 94.03 | 0.0122 | 0.991 |
| | | 313.15 | 86.95 | 0.0090 | 0.989 |
| | | 323.15 | 59.08 | 0.0105 | 0.984 |
| | Acid Orange 51 | 303.15 | 39.84 | 0.0520 | 0.977 |
| | | 313.15 | 32.58 | 0.0330 | 0.958 |
| | | 323.15 | 24.23 | 0.0214 | 0.964 |

The interaction of the acid dyes with the surface of activated carbon materials is expected to be mainly between the oxygen-free Lewis base sites, which are related to delocalized π electrons on the basal planes of the activated carbon and the free electrons of the dye molecule resulting from several aromatic rings and double bonds and negatively charged ions of these dyes (Pereira et al., 2003). The surface groups in activated carbon (carboxyl, lactone and phenol) with acid character had a negative effect on adsorption performance as indicated in Figures 6 and 7 and Tables 6 and 7. The decrease of adsorption capacity and affinity coefficient due to the fact that these acid groups attract and thus localize π electrons of the condensed aromatic sheets on the surface of the activated carbons, and at the same time they cause the steric blockage of the dye molecules (Pereira et al., 2003).

It is well known that temperature has an important role in adsorption in activated carbons, generally having a negative influence on the amount adsorbed (Ismadji and Bhatia, 2000b). The adsorption of organic compounds is an exothermic process and the physical bonding between the organic compounds and the active sites of the carbon will weaken with increasing temperature. This phenomenon was also observed in our experiments as indicated in Figures 5-7. Also, from Tables 5-7, the parameter Q_m also decreased with increasing temperature, this was consistent with the experimental data. It was evident that the Langmuir equation was valid to represent our experimental data in the whole range of concentrations and temperatures.

5. Conclusions

The adsorption isotherms of acid blue 9, acid blue 74, and acid orange 51 on activated carbon derived from teak sawdust (unmodified and modified) were obtained in this study. The adsorption isotherm data were correlated by Langmuir model, it was found that the Langmuir model could represent the adsorption data well with the correlation coefficient of R^2 more than 0.95. The surface acidity of activated carbon plays a key role in dye adsorption. Starting from the same material and using chemical treatment to modify their surface acidity without changing their pore structure, a substantial variation in dye removal capacity was observed.

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