Methylene Blue Sorption onto Oxygenated Pyrolytic Tire Char: Equilibrium and Kinetic Studies

Augustine Quek\(^1\); Kuppusamy Vijayaraghavan\(^2\); and Rajashekhar Balasubramanian\(^3\)

Abstract: A novel method is presented for pyrolyzing and activating waste tires for adsorptive removal of aqueous contaminants. The adsorption characteristics of a cationic dye (methylene blue, MB) by pyrolytic tire char were evaluated. Mechanistic insights into the adsorption of MB onto char made from pyrolyzed tires are discussed on the basis of equilibrium and kinetic studies. A comparative evaluation of the performance of un oxygenated, pyrolyzed chars (NoPPO) and oxygenated chars (P550250) is reported. Despite having similar surface areas between the oxygenated and un oxygenated chars, the adsorption capacity of the former was much higher than that of the latter. However, adsorption of MB is thermodynamically unfavorable ($\Delta G > 0$) although oxygenation lowers the free energy of adsorption. MB sorption onto P550250 is inhibited by an external film, which was not observed in the case of NoPPO. An increase in the solution temperature was found to reduce the adsorption rates of MB onto P550250 but increase the sorption capacity of NoPPO. Overall, oxygenation was found to improve the sorption of MB onto pyrolytic chars. DOI: 10.1061/(ASCE)EE.1943-7870.0000387. © 2011 American Society of Civil Engineers.

CE Database subject headings: Waste management; Tires; Adsorption; Sorption; Kinetics.

Author keywords: Pyrolysis; Tires; Methylene blue; Adsorption; Sorption; Modeling.

Introduction

Approximately 1.3 billion waste tires are produced annually worldwide (Beecham 2008). Considering such a large volume of production, there is a huge problem in dealing with waste tires. In Singapore alone, with a population of just 4.5 million, more than 25,000 t of waste tires are produced annually [National Environment Agency (NEA) 2008]. The problem of scrap tires would also be amplified in the near future as rapid urbanization and improvements in standards of living increase vehicle populations. Thus, there is an urgent need to find effective, economic, and environmentally sound solutions to treat scrap tire wastes.

One possible alternative that has been shown to be technically feasible is to pyrolyze rubber tires and use the resultant char as an adsorbent of organic compounds. An early work by Lucchesi and Maschio (1983) used pyrolyzed tire char for the adsorptive removal of acid black and orange II dyes. They showed that tire chars had higher adsorption of dyes than commercial activated carbon.

Ariyadejwanich et al. (2003) also found higher adsorption of black 5 dye on HCl-treated pyrolyzed tire char than on commercial activated carbons. In comparison with other waste materials, László et al. (1997) found nearly 10 times higher adsorption of 2,3,4-trichlorophenol on pyrolyzed tire char than on pyrolyzed rice husks. More recently, Rozada et al. (2005) compared pyrolyzed sewage sludge and tire chars and observed methylene blue (MB) adsorption capacity of the latter to be more than twice that of the former. Thus, there is a huge potential for pyrolyzed tires to be used in the removal of large aromatic compounds from solution. San Miguel et al. (1998) found significant increases in MB adsorption with increases in pyrolysis temperature.

This study uses MB as a model target contaminant that was removed from aqueous solution by oxygenated pyrolyzed tire char. MB was chosen because it is a common dye with wide applications, including textile finishing, paper coloring, hair coloring, cotton and wool dyeing, and stock marking (Vadivelan and Kumar 2005). A novel method of activation called postpyrolysis oxygenation (PPO) was used, where pyrolyzed tire char were oxygenated in situ without the use of additional heat. Surface characterizations were done on these PPO chars and on unactivated chars before they were used in batch adsorptive removal of MB. To evaluate the oxygenated chars as a possible sorbent for the removal of cationic dyes, several sorption models were fitted to sorption results to obtain sorption parameters. Both the equilibrium characteristics and transient behavior while attaining equilibrium were modeled to provide further mechanistic insights into the adsorption of MB onto the pyrolyzed tire char.

Experimental

Material

Raw scrap tire samples were obtained from a commercial recycling plant that has the technology to separate the wires from the rubber.
and fiber materials. The received scrap tire rubbers were further cut to small cubes (~1 mm) before pyrolysis.

**Pyrolysis and Activation**

Pyrolysis of scrap tire samples was done in a horizontal tubular reactor with N₂ gas flow rate of 0.6–0.8 L/min at a heating rate of 20 K/min until 823 K (550°C) was reached. This maximum temperature was held for 1 h to ensure that all pyrolytic reactions were completed. The temperature of 823 K (550°C) was chosen for further experiments on the basis of optimum results obtained, and it is the commonly accepted temperature at which pyrolysis of tires is considered completed (Williams and Besler 1995; San Miguel et al. 1998; Chen et al. 2001; Helleur et al. 2001; Quek and Balasubramanian 2009a).

The char was further activated by PPO, where 7% oxygen (by volume) was introduced into the pyrolysis furnace to oxygenate the char, after pyrolysis was completed and the temperature started to decrease. This oxygenation was carried out between 523 and 823 K (250 and 550°C), and the resulting char was named P550250. The maximum pyrolysis temperature of 823 K (550°C) was found to be optimum in terms of pyrolysis time, energy used, and char yield, based on previous results. Tire char pyrolyzed without oxygenation was also produced in a similar manner and was referred to as NoPPO. The details of the pyrolysis and activation process have been reported elsewhere (Quek and Balasubramanian 2009b).

**Char Surface Characteristics**

The ASTM D3172–07 method was used in determining the approximate amounts of moisture, volatile matter, ash, and fixed carbon for the P550250 and NoPPO char by using the Carbolite CWF 1100 furnace (Sheffield, England). The pH at zero zeta potential was measured using Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK).

**Surface Elements**

The residue samples were also analyzed using X-ray photoelectron spectroscopy (XPS) (Kratos AXIS Hsi; Kratos Inc., Manchester, UK) for surface elements [1,486.71 eV, 10 KV, 15 mA (150 W); CWF 1100 furnace (Sheffield, England). The pH at zero zeta potential was measured using Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK).

**Surface Area and Porosity**

For measurements of pore-size distributions and BET surface areas, the NOVA 4200 Multistation Anygas Sorption Analyzer (Quantachrome Instruments, Boynton Beach, FL) was used. Nitrogen adsorption isotherms were obtained at 77 K, and the BET equation used to obtain the surface areas, whereas the Barret-Joyner-Halenda (BJH) method was used to derive the pore-size distribution.

**Equilibrium and Kinetic Sorption Studies**

Each sample prepared consisted of 100 mL of solution with 100 mg of tire char and was shaken for 10–12 h at a speed of 150 rpm. For the kinetic experiments, the initial concentration of MB was 100 mg/L, whereas the initial pH of the solutions was measured and adjusted to 4.0 (±0.2) using 0.1 M of HNO₃ and/or 0.1 M of NaOH. Three different temperatures (297, 308, and 323 K) were used for the kinetic experiments in a temperature-controlled shaker. For the equilibrium experiments, MB concentrations of up to 500 mg/L were used, with initial pH of 2–7 at 297 K. For each run, at least three samples were used (triplicate); in addition, one flask of the solution with no added sorbents was used as a control.

The solutions were then filtered to remove the chars from solutions before analytical measurements were made. MB solutions were measured using an ultraviolet (UV) spectrophotometer (Digilab-Hitachi U2800) at a wavelength of 665 nm.

**Equilibrium and Kinetic Adsorption Models**

The equilibrium adsorption of MB onto tire char was analyzed using two popular isotherms equations—the Langmuir [Eq. (1)] and Freundlich [Eq. (2)] isotherms.

\[
q_e = \frac{q_m a_1 C_e}{1 + a_2 C_e} \quad (1)
\]

\[
q_e = K_F C_e^{1/n} \quad (2)
\]

where \( q_e \) (mg/g) = amount of MB adsorbed by the tire char at equilibrium; \( C_e \) (mg/L) = MB concentration in solution at equilibrium; \( a_1 \) (L/mg) = Langmuir affinity constant; \( q_m \) (mg/g) = Langmuir monolayer saturation capacity; \( K_F \) (L/g) = Freundlich capacity; and \( n = \text{affinity constant.} \)

The transportation mechanisms investigated in this paper are external film diffusion from Spahn and Schlunder (1975) and the Bangham equation (Arhoni et al. 1979). The equations for external diffusion mechanism (EDM) [Eq. (3)] and the Bangham equation [Eq. (4)] are written as follows:

\[
Ln\left(\frac{C_t}{C_o}\right) = -k_i \cdot t \quad (3)
\]

\[
q_t = k_B t^\alpha \quad (4)
\]

where \( t \) (min) = time of reaction; \( C_o \) and \( C_t \) = initial concentration (mg/L) and concentration at time \( t \), respectively; \( k_i \) (min⁻¹) = EDM diffusion coefficient; \( q_m \) (mg/g) = amount adsorbed at time \( t \); \( k_B \) (mg/g min⁻¹) = concentration-dependent diffusion factor; and \( \alpha = \text{unitless constant (less than 1).} \)

The intraparticle diffusion (IDP) model from Weber and Morris (1963) uses the same equation as Bangham’s equation but with \( \alpha = 0.5, \) assuming Fick’s equation and that the pores are far from being filled completely.

\[
q_t = k_i (t^{0.5}) \quad (5)
\]

where \( k_i \) (mg/g min⁻⁰.⁵) (with \( i = 1–3 \) = IDP diffusion rate constant; all other notations are as previously given.

Nonlinear regression was used to obtain the model constants for all the models. The correlation coefficient \( (r^2) \) was calculated, and the best fit by the model constants was determined by the highest correlation coefficient.

**Thermodynamic Parameters**

Three thermodynamic parameters of changes in enthalpy, entropy, and Gibb’s free energy \( (\Delta H, \Delta S, \Delta G) \) at constant temperature were calculated using the following relations:

\[
\Delta G = -RT \ln K \quad (6)
\]

\[
\Delta G = \Delta H - T \Delta S \quad (7)
\]

where \( R = \text{gas constant; } T = \text{temperature; and } K = \text{equilibrium constant.} \) The equilibrium constant is the ratio of percentage MB remaining in solution over percentage MB removed, or the extent of reaction. The change in entropy and enthalpy was obtained by
Table 1. Characteristics of Pyrolyzed Chars

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Pyrolyzed char (NoPPO)</th>
<th>PPO char (P550250)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>72.4</td>
<td>74.3</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.241</td>
<td>0.253</td>
</tr>
<tr>
<td>pHₚₑｃ</td>
<td>7.95</td>
<td>4.16</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>8.63</td>
<td>10.9</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>0.41</td>
<td>5.81</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>90.5</td>
<td>82.9</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>0.46</td>
<td>0.38</td>
</tr>
</tbody>
</table>

plotting the Gibb’s function ($\Delta G$) as a function of temperature ($\Delta G$ versus $T$) (Rozada et al. 2005).

Results and Discussion

Adsorbent Characteristics

Char Characteristics

Table 1 shows the several characteristics of the two chars. The surface areas were relatively low, but this is within the variations found in literature values of 19–93 m²/g (San Miguel et al. 1998; Suuberg and Aarna 2007; Ariyadejwanich et al. 2003; László et al. 1997; Helleur et al. 2001; Teng et al. 2000). The values for the surface areas shown in Table 1 have a standard deviation of ±20 m²/g.

Oxygenation of the chars under the experimental conditions did not significantly increase the surface area but increased the pore volumes. This has been shown to be attributable to an enlargement of existing pores caused by the oxidizing atmosphere rather than the creation of new pores (Suuberg and Aarna 2007). Porosity development has previously been shown to be independent of oxygen content (Zabaniotou and Stavropulos 2003) in the pyrolysis atmosphere but dependent on the degree of burn-off (mass loss). Suuberg and Aarna (2007) have also shown that pore development is independent of temperature within the range of 673–773 K for chars activated with oxygen gas.

The surface also showed a transition from basic to acidic (pHₑₚₑ) after oxygenation, indicating an increase in negative surface charges. The results show that pyrolytic tire char has a low surface area and low porosity adsorbent, but its surface chemistry changed significantly upon oxygenation. The change in surface chemistry, together with its enlargement of pores, provides a strong basis for improvement in MB sorption.

Surface Composition

The composition of the most external surface of the char particles can be seen in an XPS wide scan on the sample. Fig. 1 shows the major atomic species on the char surface. The biggest peak is the carbon peak at a binding energy (BE) of 280–295 eV, whereas the other major species are oxygen (BE = 525–540 eV) and Zn (BE = 1,021.8–1,021.9 eV). No other peaks of any significant size could be detected by this method, indicating that any functional groups must be composed of only Zn, O, C, and H atoms.

Fig. 2 shows the BE peaks for the Zn₂p electrons. Chars that were not oxygenated (NoPPO) have only one main zinc peak and did not show any zinc oxide peaks [Fig. 2(a)], whereas oxygenated chars (P550250) showed both the zinc and zinc oxide peaks [Fig. 2(b)]. Similar peaks were obtained and analyzed for the C₁s, O₁s, and N₁s atoms. Curves were also fitted for each BE according to their corresponding functional groups, which have been identified by earlier researchers (Wagner et al. 1979, 1980).

Table 2 gives the surface relative mass concentrations of these four elements, as calculated by their peak areas. No strong peaks for nitrogen could be detected (Table 2), indicating a lack of nitrogen groups on the carbon surface, and these groups are thus of no further interest for discussion. The values also strongly indicate that oxygenation of the char does indeed occur, with more oxygen content in the char at higher temperatures and longer reaction times. This observation is in agreement with the review by Puri (1971) on the formation of carbon-oxygen complexes.

The Zn₂p peak of atomic zinc at a BE of 1,021.8–1,021.9 eV and its oxide peak at 1,022.5 eV (Biniak et al. 1997) can be used to identify the extent of oxidation that PPO has on the pyrolyzed char. Fig. 2 shows the result of this fit. The char that has been oxygenated (P550250) shows a large oxide peak to the left of the main zinc peak, with the oxide peak area larger than the zinc peak. The un oxygenated char (NoPPO) shows almost no oxide peak.

Similarly, the curve fitting for the various peaks to the O₁s spectra (Wagner et al. 1979, 1980; Biniak et al. 1997) for the two char types revealed that the ZnO peak (BE = 530.4 eV) was much larger for P550250 than for the NoPPO char (530.8 versus 24.7 units). The oxygenated char also had higher proportions of C-OH and/or C-O-C groups compared with C = O groups. This suggests a higher degree of saturation and higher oxygen concentration on the surface than the unoxy genated char. Small peaks could also be fitted for chemisorbed oxygen and/or water. The presence of water in any significant amount can be ruled out, as the samples

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were dried in the oven before XPS analysis, which is also performed under a vacuum.

The C1s spectra provide further consistent evidence as shown in Table 3. Longer oxidation times increase oxygen functional groups. This is indicated by the sizes of the peaks relative to each other. The most significant increase can be seen in the pyrolyzed char that has been oxidized for 2.5 h (P550250) at decreasing temperatures. The peak corresponding to the C-O group showed a notable increase in relation to the other oxygen peaks, as well as to the main graphitic peak. Because carbidic carbon is that which is bound to a weakly electronegative element and the carbidic carbon peak areas were consistently low in all cases, they were not considered to be present in amounts that could significantly affect the surface chemistry. Table 3 shows the assignments and the binding energies for each peak, together with the normalized peak areas compared with the main graphitic peak.

**Adsorption Equilibrium**

### Effect of pH

Because solution pH is considered to be a major factor influencing sorption chemistry, different initial solution pH was used in the adsorption studies. Fig. 3 shows with error bars the percentage removal of MB at various initial pH values after 10 h, when the system is at equilibrium.

The final pH of the solution after 10 h was also measured (data not shown) and showed only slight deviation from its initial pH. The apparent higher sorption at pH = 3 and 4 was attributable to the aggregation and agglomeration of MB at low pH values (Uddin et al. 2009), thus giving a darker color for the control solution for comparison with the samples and a higher calculated adsorbed amount.

### Equilibrium Isotherms

The isotherm data for methylene blue adsorption are shown in Fig. 4 for the two adsorbents—P550250 and NoPPO. The concave curves of both lines are typical “L”-type isotherms (Limousin et al. 2007), with oxygenated char (P550250) isotherm clearly reaching a plateau at a higher level, indicating a higher sorption capacity. The Langmuir and Freundlich constants derived from the data are shown in Table 4. In general, both isotherm models fit the adsorption onto NoPPO fairly well, with the Freundlich isotherm having a slightly better fit than Langmuir for P550250. Both models also fit NoPPO better than P550250.

The theoretical maximum ($q_m$) sorption capacities for MB were 103.8 and 33.11 mg/g on P550250 and NoPPO, respectively. This is comparable to the $q_m$ of pyrolyzed tire chars of 22.2 mg/g (San Miguel et al. 1998), 32–35 mg/g (Helleur et al. 2001), and 41.0 mg/g (Rozada et al. 2005) in the literature. The results showed that PPO increased the MB sorption capacity more than threefold. Helleur et al. (2001) also found an increase in sorption capacity for oxygenated tire char. They activated pyrolyzed tire

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**Table 3. Assigned Groups’ Binding Energies and Respective Relative Areas**

<table>
<thead>
<tr>
<th>Assigned group(s)</th>
<th>Binding energies (eV)</th>
<th>Peak number</th>
<th>Relative area</th>
</tr>
</thead>
<tbody>
<tr>
<td>π − π* transitions in aromatics</td>
<td>291.2–292.1</td>
<td>1</td>
<td>5.176 7.681</td>
</tr>
<tr>
<td>COOH, COOR</td>
<td>289.3–290.0</td>
<td>2</td>
<td>1.797 5.755</td>
</tr>
<tr>
<td>Carbonyl C = O</td>
<td>287.5–288.1</td>
<td>3</td>
<td>1.575 4.587</td>
</tr>
<tr>
<td>C-O, C-O-C,</td>
<td>286.3–287.0</td>
<td>4</td>
<td>8.827 22.82</td>
</tr>
<tr>
<td>Main graphitic peak</td>
<td>284.6–285.1</td>
<td>5</td>
<td>100 100</td>
</tr>
<tr>
<td>Carbidic</td>
<td>282.6–282.9</td>
<td>6</td>
<td>0.076 0.174</td>
</tr>
</tbody>
</table>

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**Table 2. Quantification of Surface Elements Based on Peak Areas by XPS**

<table>
<thead>
<tr>
<th>Mass concentration (%)</th>
<th>Zn</th>
<th>O</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>NoPPO</td>
<td>1.57</td>
<td>3.66</td>
<td>94.0</td>
<td>0.76</td>
</tr>
<tr>
<td>P550250</td>
<td>6.79</td>
<td>8.85</td>
<td>83.7</td>
<td>0.65</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Zn2p spectra curve fitting for (a) NoPPO char (showing only the zinc peak) and (b) P550250 char (showing a large oxygen peak)

**Fig. 3.** Percentage removal of copper and MB by P550250 and NoPPO at various initial pH [initial concentration = 100 mg/L (0.313 mol/L) at 297 K]
char with 2% oxygen above 973 K and found an increase from 32–35 mg of MB per gram of char to 60 mg/g. However, their apparent increase in MB capacity was lower than that found in this study because of the differences in pyrolysis conditions. They oxidized their carbons a higher temperature, which was found to achieve a greater degree of burn-off with decreased microporosity (Suuberg and Aarna 2007), thus decreasing sorption capacities.

The performance of the tire chars was compared with that of commercial activated carbons. P550250’s Langmuir sorption capacity ($q_m$) was particularly comparable. Yerner et al. (2008) modeled MB sorption onto Norit SA3 powdered activated carbon and Nuchar WWH granulated activated carbon and obtained Langmuir sorption capacities of 91 and 21.5 mg/g, respectively. Ghasemi and Asadpour (2007) sorbed MB with an initial concentration of 800 mg/L onto charcoal activated carbon and obtained a maximum removal of 69.8 mg/g. They also observed higher MB removal with higher temperatures and obtained positive values for the enthalpy and entropy of MB sorption, a trend similar to what was seen for NoPPO in this study. In investigating the removal of MB from wastewaters by activated carbon, Wang et al. (2005) used Calgon’s coal-based and coconut shell–based activated carbon. They achieved an MB removal of 177.7 mg/g for F100, 181.1 mg/g for coal-based activated carbon, and 217.3 mg/g for coconut shell–based activated carbon. Yasin et al. (2007) also used coconut shell–based activated carbon for MB sorption and obtained 41.8 mg/g of removal for the initial MB concentration of 100 mg/L and 17.8 mg/g of removal for 50 mg/L of the initial concentration.

In this study, although removal capacities are dissimilar, the binding coefficients ($K_L$) are very close with 0.041 for P550250 and 0.039 for NoPPO (Table 4). This is also seen for the Freundlich constant ($n$), with values of 2.67 for P550250 and 2.59 for NoPPO (Table 4). The physical significance of these values is that MB binds with similar strength to both P550250 and NoPPO. Although similar binding processes occur on the surface of both chars, the total sorption capacities are very different. Any difference in sorption mechanism should be attributed to the transient states while achieving equilibrium.

**Thermodynamics**

The three thermodynamic parameters of changes in enthalpy, entropy, and Gibb’s free energy ($\Delta H$, $\Delta S$, $\Delta G$) were calculated and are given in Table 5. The plots from which the $r^2$ values were derived are shown in Fig. 5. Table 5 shows that the adsorption of methylene blue onto tire chars was not spontaneous. However, increasing the solution temperature increases the spontaneity of methylene blue adsorption onto NoPPO char but not for P550250. This observation points to very different adsorption mechanisms between oxygenated and unoxygenated tire chars.

Another difference is the enthalpy of adsorption between the two chars. The adsorption onto oxygenated char (P550250) is exothermic but highly endothermic for unoxygenated char (NoPPO). The enthalpy changes suggest that for NoPPO, chemisorption is predominant (> 30 kJ/mol) (Rozada et al. 2005; El-Khaiary 2007), whereas physisorption occurs for P550250 (negative enthalpy).

A third difference is in the entropy of adsorption. Methylene blue adsorption onto P550250 showed a decrease in entropy, indicating a reduction in disorder. This may seem counterintuitive to our current understanding of adsorption, where (hydration) water molecules covering the surface as well as surrounding the adsorbate molecules are released upon adsorption. However, the outer shell of water molecules surrounding the adsorbate may not be released in the case of physisorption. The higher sorption capacity of P550250
Table 4 also means that more molecules of MB are aggregated on its surface, thus decreasing entropy.

Adsorption Kinetics

The kinetics of adsorption for MB onto pyrolytic char is shown in Fig. 6. The increase in solution temperature causes a decrease in the rate and amount of MB adsorption onto P55250 but causes an increase for NoPPO. For P550250, the sorption plateaus at 350 min regardless of temperature. For NoPPO, the time to achieve equilibrium increased with increasing temperature, from less than 100 min at 297 K to more than 300 min at 323 K. NoPPO at 323-K solution also seemed to reach a similar adsorption capacity as P550250 at 297 K. This could be caused by the formation of surface sorption sites on NoPPO at higher temperatures, increasing its capacity. Therefore, the oxygenation process provided a rather different sorption mechanism compared with unxoygenated chars. These differences are can be analyzed through modeling, and the different results are reflected in the various kinetic model constants (Tables 6 and 7).

Adsorption occurs through the mass transfer of the adsorbate from the bulk solution to the surface of the solid adsorbent. Therefore, the transient behavior of adsorption can be divided into three distinct stages: molecular diffusion, intraparticle transport, and adsorbate attachment (El-Khaiary 2007).

The differences in the transient behaviors of MB sorption onto P550250 and NoPPO can be understood as different kinetic rates of these three stages for different adsorbates and adsorbents. Modeling can be done to elucidate the rates and relative importance of each stage of adsorption process.

External Mass Diffusion and Internal Pore Transport

Adsorption processes controlled by the external resistance show linearity in a plot of In C versus time. For adsorption of MB onto P550250, only the initial 3–6 h is limited by film diffusion. Increasing the temperature decreases the film diffusion rate and thus increases the difficulty for adsorption of MB during the first 6 h, whereas MB adsorption onto NoPPO char seems to be limited by film diffusion for only the first hour (Table 6). One reason for this observation is that there are much fewer sorption sites on NoPPO than on P550250; hence, fewer MB molecules are sorbed on NoPPO than on P550250. However, the fits for P550250 are much better than for NoPPO.

Table 6 also shows the results of the fitting of the Bangham equation. Although the Bangham equation can describe by more than one mechanism, it was derived by assuming that the adsorption activation energy varies logarithmically with the amount adsorbed. According to this concept, the Bangham equation is a kinetic expression corresponding to the Freundlich equation, which implies a heat of adsorption varying logarithmically with the amount adsorbed. It can also be interpreted as intraparticle diffusion kinetics (Kavitha and Namasivayam 2007), where adsorption rates are controlled by diffusion in the pores of the adsorbent. From the results in Table 6, there is a similar trend of decreasing $k_B$ and increasing $\alpha$, showing that pore diffusion is significant but

<table>
<thead>
<tr>
<th>Temperature</th>
<th>EDM constants</th>
<th>Bangham constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_i$ (min$^{-1}$)</td>
<td>Condition</td>
</tr>
<tr>
<td>P550250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297 K</td>
<td>0.0021</td>
<td>Up to 180 min</td>
</tr>
<tr>
<td>308 K</td>
<td>0.0013</td>
<td>Up to 360 min</td>
</tr>
<tr>
<td>323 K</td>
<td>0.0008</td>
<td>Up to 360 min</td>
</tr>
<tr>
<td>NoPPO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297 K</td>
<td>0.0008</td>
<td>Up to 60 min</td>
</tr>
<tr>
<td>308 K</td>
<td>0.0014</td>
<td>Up to 60 min</td>
</tr>
<tr>
<td>323 K</td>
<td>0.0021</td>
<td>Up to 60 min</td>
</tr>
</tbody>
</table>

Fig. 6. Adsorption of MB with time and temperature [initial concentration = 100 mg/L (0.313 mol/L)]
decreases with temperature increase. The $R^2$ fits for the EDM and Bangham coefficients are shown in Fig. 7.

For IPD, there are three distinct steps for the adsorption onto P550250 [Fig. 8(a)] but only two for the adsorption onto NoPPO [Fig. 8(b)]. These are shown as individual straight lines drawn on the figures, with their correlation coefficients and gradient values. For P550250, the first step is a slow step, followed by a relatively faster transition stage and then an almost flat plateau portion. Stage 1 is attributed to overcoming the thin film on the adsorbent external surface, as shown in the EDM results (Table 7). Stage 2, exhibiting fast removal, is ascribed to the intraparticle diffusion, stimulating further migration of adsorbate from the liquid phase to the adsorbent internal surface. Stage 3, the plateau section, shows the final equilibrium state. Temperature has a negative effect for all three stages, which is in agreement with earlier results (Tables 7). This is similar to the results of El-Khaiary (2007), who applied the IPD model to MB adsorption on nitric acid–treated water hyacinth and found three distinct regions. El-Khaiary concluded that the three regions correspond to rapid surface loading, pore diffusion, and equilibrium.

For NoPPO, the two stages could correspond to intraparticle diffusion and adsorption onto surface sites (Tables 7 and Fig. 8), with the rate-limiting step likely to be adsorption because activation of the char was incomplete. This provides further evidence that the adsorption onto oxygenated pyrolyzed tire char follows a distinctly different pathway compared with unoxygenated pyrolyzed tire.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Stage 1</th>
<th></th>
<th>Stage 2</th>
<th></th>
<th>Stage 3</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$k_1$ (mg/mg min$^{-0.5}$)</td>
<td>$r^2$</td>
<td>$k_2$ (mg/mg min$^{-0.5}$)</td>
<td>$r^2$</td>
<td>$k_3$ (mg/mg min$^{-0.5}$)</td>
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<td>P550250</td>
<td></td>
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<tr>
<td>297 K</td>
<td>0.0151</td>
<td>0.941</td>
<td>0.0242</td>
<td>0.925</td>
<td>0.0028</td>
</tr>
<tr>
<td>308 K</td>
<td>0.0146</td>
<td>0.956</td>
<td>0.0199</td>
<td>0.917</td>
<td>0.0016</td>
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<tr>
<td>323 K</td>
<td>0.0124</td>
<td>0.896</td>
<td>0.0159</td>
<td>0.961</td>
<td>0.0009</td>
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<tr>
<td>NoPPO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>297 K</td>
<td>0.0077</td>
<td>0.964</td>
<td>0.0019</td>
<td>0.960</td>
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</tr>
<tr>
<td>308 K</td>
<td>0.0154</td>
<td>0.901</td>
<td>0.0047</td>
<td>0.932</td>
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<tr>
<td>323 K</td>
<td>0.0195</td>
<td>0.910</td>
<td>0.0068</td>
<td>0.890</td>
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Fig. 7. (a) EDM correlations for P55250 at various temperatures; (b) Bangham correlations for P55250 at various temperatures; (c) EDM correlations for NoPPO at various temperatures; (d) Bangham correlations for NoPPO at various temperatures.
The lack of a third stage in the adsorption process for NoPPO char, compared with the three stages of P550250 from the IPD model, points to a dependency on oxygenated sites on the tire char. Therefore, based on the evidence presented so far, oxygenation of the char surface produces adsorption sites necessary for MB sorption. Sorption of MB onto P550250 is thus limited by external factors such as mass transfer and film thickness, which showed distinctive stages in the IPD model. Unoxygenated chars (NoPPO) are not limited by external factors but rather by the amount of sorption sites. Therefore, NoPPO does not show distinct rate-limiting stages, as shown in Fig. 8(b).

**Conclusions**

Oxygen can be used in the activation of char to produce adsorption sites. Although oxygenated chars showed higher adsorption capacities than unoxygenated ones, the binding affinities were similar. Their equilibrium capacities were also similar at high solution temperatures (323 K). Increasing solution temperatures increased the MB sorption capacity of unoxygenated chars significantly but not for oxygenated chars.

Significant differences in sorption mechanisms were found between oxygenated and unoxygenated chars. P550250 showed an exothermic sorption reaction for MB, whereas NoPPO’s sorption was endothermic, with P550250 having a lower Gibb’s free energy of sorption than NoPPO at room temperature. Thus, sorption onto oxygenated char is thermodynamically more favorable than onto unoxygenated tire chars. Adsorption onto P550250 follows three distinct steps, whereas NoPPO only has two. This information has significant engineering implications such that knowledge of various design parameters (pH, temperature, reactor type, etc.) is necessary to construct a working treatment unit. Because waste tires are abundant in any urban center, the use of waste tire chars would not only be cost-effective but would also help reduce solid waste.

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**Fig. 8.** IPD plot for adsorption of methylene blue onto (a) P550250) and (b) NoPPO [initial concentration = 100 mg/L (0.313 mol/L)]