



# Simultaneous adsorption of methyl red and methylene blue onto biochar and an equilibrium modeling at high concentration



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## HIGHLIGHTS

- A multi-component isotherm model was built.
- The model was verified by methyl red and methylene blue adsorption onto biochar.
- Validity of the model was explored.
- Adsorption also met with the model well with more solutes.
- Parameter  $n$  in this model could describe the relationship among adsorbates.

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## ABSTRACT

Methyl red, methylene blue and biochar were used to investigate simultaneous adsorption of dyes onto low-cost adsorbent at different concentrations combinations. Langmuir mixed model could describe the adsorption well at low concentrations. However, it could not describe the adsorption anymore when concentrations of methyl red and methylene blue were higher than 255 and 300 mg L<sup>-1</sup> respectively with 0.5 g L<sup>-1</sup> biochar loading. A new model on the interaction among adsorbed adsorbates at equilibrium was developed. It could describe the adsorption at high concentrations well. According to the experimental results, interaction among dyes molecules would replace the competition onto adsorbent to be the main factor influencing adsorption when amount of adsorbed adsorbates were higher than those required to form a monolayer on all the adsorbing sites of adsorbent. The model was further verified by adsorption with other solute such as glucose or NaCl in solution.

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## 1. Introduction

To cut down on the amount of commercial adsorbent consumption in disposal of dyeing effluent, various low-cost adsorbents have been developed (Rafatullah et al., 2010; Sharma et al., 2011; Noroozi and Sorial, 2013). These adsorbents exhibited low adsorption capacity for dye compared with commercial adsorbents such as activated carbon and zeolite (Rafatullah et al., 2010; Sharma et al., 2011; Kearns et al., 2014). They could remove dye from effluent partly and consequently, reduce the commercial adsorbent consumption in following treatment. However, the removal efficiency was normally unclear which heavily weaken the feasibility of these adsorbents (Noroozi and Sorial, 2013). Adsorption

capacities of these adsorbents have been investigated repeatedly in laboratory (Wang et al., 2013; Kearns et al., 2014). However, these investigations were carried out at low concentration which is far from application. Dye concentration in these researches was normally lower than 200 mg L<sup>-1</sup>. Different from laboratorial research, dyeing effluent normally contained high concentration of dye (Kyzas et al., 2011; Khatri et al., 2015; Rosa et al., 2015; Piccin et al., 2016). If pigmentation ratio was 60% with liquor ratio being 5:1 and owf being 4%, a single dye concentration in effluent from dyeing procedure would be 3.2 g L<sup>-1</sup>. According to former research, the pigmentation concentration might be higher (Noroozi and Sorial, 2013). In application, liquor ratio and owf could also be higher. Even taking into account effluents from other processes in dyeing industry, the final dyes concentrations in effluent would be definitely much higher than 300 mg L<sup>-1</sup>. Investigation at low concentration was hard to guide the application.

At the same time, these researches were carried out in a single-

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solute system which was also different from application. Dyeing effluent normally contained more than one species of dye in high concentration (Mahmoud et al.; Rao and Rao, 2006; Wang et al., 2013; Kearns et al., 2014; Yang and Jiang, 2014; Sun et al., 2015; Lonappan et al., 2016). Based on some classical isotherms, some mixed adsorption isotherms had been developed to describe the simultaneous multi-adsorbate adsorption (Prosser and Franses, 2003; Esteves et al., 2008; Bjørner et al., 2013; Chakraborty and Sun, 2014; Park et al., 2016). Liu had comprehensively reviewed these models and pointed out that these isotherms were not suitable for adsorption at high adsorbates concentrations for the drawback in basic assumption (Liu, 2015). Till now, most investigation was performed in dilute solution with zeolite and activated carbon which was definitely far from the application of low-cost adsorbents in dyeing effluent. At the same time, adsorbates in these researches were definitely different from dye. The results achieved by ion or gas could not roughly applied on dye.

In this paper, a model was built based on the Gibbs free energy change at chemical equilibrium to describe the adsorption of methyl red and methylene blue onto biochar simultaneously and verified at different concentrations. The model was developed based on equilibrium so that some factors influencing adsorption kinetics could be ignored. It made the model convenient in application. Biochar is the solid residue in pyrolysis or gasification of biomass (Ahmad et al., 2014). With the similar carbonaceous and porous structure as activated carbon, biochar is thought to be the potential substitute for activated carbon. Adsorption of pollutants onto biochar has been investigated repeatedly (Mahmoud et al.; Ahmad et al., 2014; Yang and Jiang, 2014; Sun et al., 2015; Lonappan et al., 2016). So, biochar was used as the adsorbent in this investigation. Methyl red and methylene blue were the model dyes in researches and were both widely applied in dyeing. They might exist in dyeing effluent in high amount simultaneously.

## 2. Methods

### 2.1. Materials

Woody biochar (0.5 mm in diameter, sieved) was the by-product of gas production through a fast pyrolysis of sawdust at 800 °C in cyclone furnace with a 0.35 water flow equivalence ratio. Biochar was washed in 100% ethanol solution with 2% w v<sup>-1</sup> (weight to volume) at 30 °C and 120 rpm (rotation per min) for 3 h. After solid/liquid separation, liquid phase and suspended matter were removed. Biochar was then washed by deionized water repeatedly till there was no suspended matter could be observed. Then, biochar was dried at 105 °C (Fig. A.1). Main characteristics of pore structure of treated biochar were 4.936 m<sup>2</sup> g<sup>-1</sup> in S<sub>BET</sub>, 0.016 cm<sup>3</sup> g<sup>-1</sup> in V<sub>t</sub>, 0.0019 cm<sup>3</sup> g<sup>-1</sup> in V<sub>mic</sub> and 12.307 nm in D<sub>p</sub>.

Methyl red (CAS: 493-52-7, MR) and methylene blue (CAS: 7220-79-3, MB) were analytical reagents.

Adsorption of dyes onto biochar was carried out at 30 °C, 120 rpm for 4 h. After adsorption, residual dye concentration in solution was detected under alkaline condition (diluting the sample by 0.05% NaOH) so that detection of MR (438 nm) and MB (672 nm) would not influence each other (Fig. A.2). Adsorbed amount of dyes was calculated by the difference between initial and equilibrium concentrations in solution. Determination was performed with spectrophotometer (UV-800s uv/vis, Yuanxi, Shanghai). Degree of accuracy was 1 × 10<sup>-3</sup>. Experiment was repeated for 5 times. As shown in following Tables, deviations were all lower than 5%. So, to facilitate calculation, means were used in modeling.

### 2.2. Modeling

According to Gibbs free energy change at chemical equilibrium, adsorption of *i* dyes onto biochar should be:

$$\Delta G_i^0 + \Delta G_{i+1}^0 + \dots = RT \ln \frac{\alpha_{si}}{\alpha_{li}} + RT \ln \frac{\alpha_{s(i+1)}}{\alpha_{l(i+1)}} + \dots \quad (1)$$

where:  $\Delta G$  is the standard change in Gibbs free energy.  $T$  is the temperature.  $R$  is gas constant.  $i = 1, 2, 3, \dots$ .  $\alpha_s$  is the activity of dye molecule adsorbed.  $\alpha_l$  is the activity of dye in solution.

Because  $\alpha = \gamma \cdot q_e$  or  $\gamma \cdot c_e$ , above equation could be converted into:

$$\Delta G_i^0 + \Delta G_{i+1}^0 + \dots = RT \ln \frac{\gamma_{si} q_{ei}}{\gamma_{li} c_{ei}} + RT \ln \frac{\gamma_{s(i+1)} q_{e(i+1)}}{\gamma_{l(i+1)} c_{e(i+1)}} + \dots \quad (2)$$

where:  $\gamma$  is activity coefficient,  $q_e$  is concentration of adsorbed adsorbate (mg g<sup>-1</sup> or mmol g<sup>-1</sup>) and  $c_e$  is concentration of adsorbate in solution (mg L<sup>-1</sup> or mM) at equilibrium.

To simplify the modeling, it is assumed that there are two adsorbates in adsorption. The equation can further be converted into:

$$-\ln \frac{\gamma_{s1}}{\gamma_{l1}} - \ln \frac{\gamma_{s2}}{\gamma_{l2}} + \frac{(\Delta G_1^0 + \Delta G_2^0)}{RT} = \ln \frac{q_{e1}}{c_{e1}} + \ln \frac{q_{e2}}{c_{e2}} \quad (3)$$

At equilibrium with a specific combination of dyes concentrations (cs), all parameters in above equation would be certain. To define:

$$A = -\ln \frac{\gamma_{s1}}{\gamma_{l1}} - \ln \frac{\gamma_{s2}}{\gamma_{l2}} + \frac{(\Delta G_1^0 + \Delta G_2^0)}{RT} \quad (4)$$

The equation can be simplified to:

$$\ln \frac{q_{e1}}{c_{e1}} + \ln \frac{q_{e2}}{c_{e2}} - A = 0 \quad (5)$$

Assuming adsorbates molecules should be adsorbed onto adsorbent as much as possible, interaction between dye 1 molecules and dye 2 molecules was homogeneous and  $n$  mol change in adsorbed dye 1 caused by one mol adsorbed dye 2. Then,  $q_{e1} + n \cdot q_{e2}$  would be the adsorbed amount of dyes molecules which could occupy the maximum possible adsorption sites in adsorption at the equilibrium for a specific combination of dyes concentrations (Fig. 1). In another word, the Lagrange multiplier equation of  $q_{e1} + n \cdot q_{e2}$  and Equation (5) which is:

$$L(q_{e1}, q_{e2}) = q_{e1} + n q_{e2} + \lambda \left( \ln \frac{q_{e1}}{c_{e1}} + \ln \frac{q_{e2}}{c_{e2}} - A \right) \quad (6)$$

would have solution at a specific combination of dyes concentrations. To achieve the  $q_{e1}$  and  $q_{e2}$  at a specific combination of dyes concentrations, partial derivatives of Equation (6) would be Equations (7) and (8):

$$L_{q_{e1}} = 1 + \lambda \left( \frac{1}{q_{e1}} + \frac{1}{c_{e1}} \right) = 0 \quad (7)$$

$$L_{q_{e2}} = n + \lambda \left( \frac{1}{q_{e2}} + \frac{1}{c_{e2}} \right) = 0 \quad (8)$$

Equations (7) and (8) can be further converted to:

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