Adsorption kinetics and isotherm of methylene blue by thermally treated alum-based water treatment plant sludge

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A B S T R A C T

This paper describes the sorption kinetic and isotherm of methylene blue (MB) by thermally treated alum sludge (TAS) at the laboratory scale. Kinetics study was conducted by varying initial concentrations of MB (50, 150 and 250 mg/L) and contact time (30, 60, 120 and 180 min) whereas adsorption isotherm was investigated at various initial concentrations (10, 50, 100, 200, 300 and 400 mg/L) at constant temperature (25°C), contact time and agitation speed. Lagergren, Ho and McKay and intra-particle diffusion kinetics modes were applied to the experimental data while the adsorption isotherms are described by Langmuir and Freundlich and Temkin isotherm models. The results showed that sorption kinetics and isotherm of MB were best described by Ho and McKay kinetics model and Langmuir isotherm model, respectively. The maximum adsorption capacity (qmax) obtained from Langmuir plot was 25.445 mg/g. It can be concluded the adsorption of MB by TAS is monolayer adsorption.

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1. Introduction

There is an increasing in disposal of hazardous organic compounds into the environment (Aksu, 2005). Wastewaters contaminated by synthetic dyes such as methylene blue (MB) are dangerous to human and environment as this pollutant may cause critical diseases to human and the intense color of dyes will interrupt the photosynthesis process (Crini, 2006). Therefore, reducing the synthetic dyes concentration to the safety limit in the effluent of the wastewater is highly required. The decolorization of dye by adsorption using cheap and abundantly available solid adsorbents is the flexible and cost-effective method. Nevertheless, the hazardous limits of the adsorbents are also highly concerns due to their impacts on the environment (Ahmed, 2016). Large amount of residual sludge is generated from drinking water processing systems which cause decreasing of landfill (Babatunde and Zhao, 2007). Reuses of water treatment plant sludge for adsorptions of heavy metals (Zhou and Haynes, 2011), phosphorus (Babatunde and Zhao, 2010) and sulphur dioxide gas (Sirisha et al., 2012) have been reported. Reusing of waste materials as adsorbents for example water treatment plant sludge could be a good alternative for removal of dyes. Md Nor et al. (2014) have applied dewatered alum sludge to remove Remazol blue R dye, which is a cationic dye.

Various techniques have been used for modification or treatment of adsorbents to increase the adsorption capacity. Conventional heating or microwave heating will strongly affect the physical and chemical properties of a material (Ahmed, 2016). Consequently, numerous researches have applied this simple technique to modify adsorbent to increase the uptake of sorbate via chemisorption, physisorption, ion exchange, complexation or...
physico-chemisorption interactions (Smiljanić et al., 2010; Kapnisti et al., 2015).

The aim of this study is to investigate adsorption kinetics and isotherm of MB by thermally treated alum-based (TAS) water treatment plant sludge. Kinetics models of Lagergren (1898), Ho and McKay (1999), and intra-particle diffusion, and isotherm models of Langmuir, Freundlich and Temkin (Levya-Ramos et al., 1995) were employed to evaluate the adsorption data.

2. Materials and methods

2.1. Preparation of adsorbents

Drinking water plant sludge cake was obtained from a local drinking water treatment plant. It was dried at 105 °C for 24 h, cooled to room temperature, crushed and ground by a mortar. Then, the dried sludge was heated at 800 °C for 7 h in a muffle furnace, cooled to room temperature and sieved to particle size between 100 to 150 μm.

2.2. Preparation of adsorbate

MB stock solution (1000 mg/L) was prepared by dissolving accurate amount of MB (3, 9-bis dimethylaminopheno thionium chloride) (Merck, Germany) in ultrapure water. Different concentrations (10, 50, 100, 200, 300, and 400 mg/L) of MB solutions were prepared by dilution using ultrapure water. pHs of the solutions were adjusted to pH 10 using 0.1 M of NaOH solution.

2.3. Adsorption kinetics and isotherm

For adsorption kinetic study, various contact time (30, 60, 120 and 180 min) and initial concentrations of MB (50, 150 and 250 mg/L) were employed, while for adsorption isotherm study, initial concentrations of MB were varied from 10, 50, 100, 200, 300 and 400 mg/L and was applied at 180 min of contact time.

The equilibrium adsorption was performed in 250 mL Erlenmeyer flasks containing 0.1 g of thermally treated alum-based water treatment plant sludge (TAS) and 20 mL of MB solution (prior adjusted to pH 10) with desired concentration. The mixture was agitated in a water bath shaker with a speed of 180 rpm at 25°C. Subsequently, the mixture was filtered using a Whatman filter paper No. 3. Concentration of MB in the filtrate was determined by UV-VIS spectrophotometer at the absorption wavelength of 665 nm. All the adsorption experiments were conducted in duplicates. The amount of methylene blue adsorbed per unit mass of TAS i.e. adsorption capacity was calculated using Eq. 1.

\[ q = \frac{(C_i-C_f) \times V}{m} \]  

where \( C_i \) (mg/L) and \( C_f \) (mg/L) are initial and final concentrations of MB, respectively, \( V \) (L) is the volume of MB solution, and \( m \) (g) is the amount of TAS used. Finally, the data was fitted into Langmuir, Freundlich, and Temkin (Levya-Ramos et al., 1995) models.

3. Results and discussion

3.1. Adsorption study

To investigate the adsorption kinetics of MB by TAS, Lagergren (1898), Ho and McKay (1999), and intra-particle diffusion models were used to evaluate the experimental data.

Lagergren (1898) kinetics model: The linear equation form of the Lagergren (1898) model is described as follows (Eq. 2):

\[ \log(q_t - q_e) = \log(q_e) - \frac{k_1}{2.303} t \]  

where \( q_t \) (mg.g\(^{-1}\)) is the adsorption capacity at time \( t \), \( q_e \) (mg.g\(^{-1}\)) is the adsorption capacity at equilibrium time, \( k_1 \) is the Lagergren (1898) rate constant (min\(^{-1}\)). The \( (q_t-q_e) \) versus \( t \) plot was employed to calculate the constant of Lagergren (1898) kinetics model and presented in Table 1.

3.2. Ho and Mckay kinetics model

Eq. 3 shows the Ho and McKay (1999) linear equation.

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

where \( q_t \) (mg.g\(^{-1}\)) is the adsorption capacity at time \( t \), \( q_e \) (mg.g\(^{-1}\)) is the adsorption capacity at equilibrium time, \( k_2 \) (g.mg\(^{-1}\).min\(^{-1}\)) is the Ho and McKay (1999) rate constant. The kinetics parameter of Ho and McKay (1999) was calculated from the plot of \( t/q_t \) versus \( t \) for the adsorption of MB by TAS.

Intra-particle diffusion kinetics model: The intra-particle diffusion kinetics model (Eq. 4) could determine the steps that controlled the rate of the adsorption process which include (a) molecular diffusion from the bulk solution to a film layer surrounding the adsorbent particle; (b) diffusion from the film to particle surface; (c) migration inside the adsorbent particle; and (d) adsorption uptake (chemisorption, physisorption, ion exchange or complexation interaction). Ghasemi et al. (2016) suggested that the rate of the adsorption process is controlled by the slowest step (Ghasemi et al., 2016).

\[ q_t = k_d t^{1/2} + C \]  

where \( q_t \) (mg.g\(^{-1}\)) is the adsorption capacity at time \( t \), \( k_d \) (mg.g\(^{-1}\).min\(^{0.5}\)) is the intra-particle diffusion rate constant and \( C \) is the intercept. The constant of the intra-particle diffusion kinetics and intercept were determined from the plot of \( q_t \) versus \( t^{1/2} \).

Table 1 shows the constants obtained from the kinetics equations (2 to 4). Figs. 1, 2 and 3 show the experimental data evaluated by Lagergren (1898),
Ho and McKay (1999) and Intra-particle diffusion equations, respectively. The results revealed that experimental data was best fitted into Ho and McKay (1999) kinetics model as indicated by the highest R² values. Besides that, the calculated adsorption capacity by Ho and McKay (1999) model is close to experimental adsorption capacity which is 25.90 mg·g⁻¹.

Table 1: Parameters of adsorption kinetics of MB by TAS

| Model               | Parameter            | Concentration (mg/L) |
|---------------------|----------------------|-----------------------|
| Lagergren (1898)    |                      |                       |
|                     | k (min⁻¹)            | 0.03487, -0.0309      |
| Ho and McKay (1999) |                      |                       |
|                     | k (g·mg⁻¹·min⁻¹)     | 0.3174, 0.0019        |
|                     | R²                   | 0.4306, 0.9833        |
| Intra-particle      | k (mg·g⁻¹·min⁻¹)     | 1.00, 0.9988          |
| diffusion           | R²                   | 0.9280, 0.9665        |

Langmuir isotherm model: This isotherm model suggests the monolayer adsorption of sorbate molecules on a homogeneous surface of sorbent with a finite number of adsorption sites, without any interaction between adsorbed molecules (Agarwal et al., 2016). Eq. 5 shows the linear form of Langmuir isotherm model:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_mR_L}
\]

where \(C_e\) (mg/L) is the equilibrium concentration of methylene blue, \(q_e\) (mg/g) is the amount of methylene blue at equilibrium, \(q_m\) (mg/g) is the Langmuir constant related to adsorption capacity and \(R_L\) (L/mg) is the Langmuir constants related to adsorption energy.

To explain the characteristics and feasibility of Langmuir isotherm, the equilibrium parameter (R_i) value is necessary to evaluate the adsorption feasibility. The R_i value may become larger than 1, equal to 1, equal to 0 and in range of 1 to 0, showing that the adsorption is unfavorable, linear, irreversible and favorable, respectively (Agarwal et al., 2016).

\[
R_L = \frac{1}{1 + R_iC_i}
\]

3.3. Adsorption isotherms

The isotherm models of Langmuir, Freundlich and Temkin (Levya-Ramos et al., 1995) were used to investigate the adsorption capacity and examined the abilities of the isotherm models to accurately describe the adsorption process.

3.4. Freundlich isotherm model

The Freundlich isotherm assumes the multilayer adsorption of sorbate molecules on heterogeneous surface of sorbent with non-uniform distribution of adsorption heat and affinities (Agarwal et al., 2016). The linear equation form of Freundlich isotherm model is represented by Eq. 7.

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]

where \(k_f\) is the adsorption capacity, \(1/n\) is the adsorption intensity. The \(n\) value indicates the favorable adsorption if \(n\) value is larger than 1.
3.5. Temkin isotherm model

This isotherm model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly with surface coverage. The linear equation form of Temkin isotherm model is represented in Eq. 8 (Dada et al., 2012).

\[ q_e = \frac{R}{b} T \ln A_T + \frac{R}{b} T \ln C_e \]  
\[ B = \frac{R}{b} T \]  

where \( A_T \) (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy, \( B \) (kJ/mol) is the Temkin constant related to the heat of sorption, \( T \) (K) is the absolute temperature and \( R \) (8.314x10^{-3} kJ/mol.K) is the gas constant.

The experimental data was evaluated by the isotherm models. Table 2 presents the constants obtained from the equations while Fig. 4, 5 and 6 show the plots of the Langmuir, Freundlich and Temkin isotherm models (Levya-Ramos et al., 1995), respectively.

The results revealed that the experimental data was best fitted by Langmuir isotherm model as indicated by the highest \( R^2 \) value (0.9721). Therefore, the adsorption of MB by TAS is monolayer adsorption. The value of \( R_l \) was 0.0516 which is between 0 and 1, suggesting that the adsorption of MB by TAS is a favourable process.

Table 2: Parameters of adsorption isotherms of MB by TAS (Levya-Ramos et al., 1995)

| Isotherm   | Parameter          | Value  |
|------------|--------------------|--------|
| Langmuir   | \( q_m \) (mg/g)   | 25.445 |
|            | \( K_L \) (L.mg⁻¹) | 0.0734 |
|            | \( R^2 \)          | 0.9721 |
|            | \( R_l \)          | 0.0516 |
| Freundlich | \( n \)            | 2.917  |
|            | \( R^2 \)          | 0.9879 |
| Temkin     | \( B \) (kJ/mol)   | 3.2527 |
|            | \( A_T \) (L.mg⁻¹) | 6.0052 |
|            | \( R^2 \)          | 0.9504 |

4. Conclusion

In this study, the kinetics and isotherm adsorption of MB by TAS were investigated. The kinetic adsorption complied well with Ho and McKay (1999) kinetics model as indicated by the highest \( R^2 \) value. Langmuir isotherm model produced the best for equilibrium data with the \( q_{max} \) of 25.445 mg/g, and it can be said that the adsorption of MB by TAS is a monolayer adsorption process.

Fig. 4: Langmuir isotherm plot for adsorption of MB using TAS

Fig. 5: Freundlich isotherm plot for adsorption of MB using TAS

Fig. 6: Temkin isotherm model plot for adsorption of MB using TAS

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