# Kinetic Models for the Sorption of Methylene Blue From Aqueous Solution by Molecularly Imprinted Polymers

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**Abstract**

The research examined the effect of concentration on Methylene Blue (MB) adsorption by using Molecularly Imprinted Polymer (MIP). The experimental data were analyzed by using pseudo-first-kinetic, pseudo-second-kinetic and particle diffusion models. From the experiment, it could be seen that the MB adsorption using MIP decreased with increasing dye initial concentration. The adsorption kinetic data of MB on MIP was well described by a first-second-order model, with the kinetic constants in the range of 0.037- 0.067 $min^{-1}$. In addition, the results also indicated that the intra-particle diffusion was not the rate limiting step in the MB adsorption process.

**Keywords:** adsorption, dye, kinetics, methylene blue, molecularly imprinted polymer

## 1. Introduction

The widespread application of dyes in textiles, printing, dyeing, and food plants has produced a large amount of dye wastewater. Since some dyes and their degradation products may be carcinogens and toxic, the removal of dyes from wastewater becomes an important issue in the environmental protection. Moreover, dyes in wastewater can obstruct light penetration and it is highly visible and unacceptable, which is not good to water life.

Various methods of dye removal from water and wastewater including oxidation (Kang, Liao & Po, 2000; Lucas & Peres, 2006; Shu & Hsieh, 2006), biological treatment (Cristóvão, Tavares, Ribeiro, Loureiro, Boaventura & Macedo, 2008; dos Santos, Cervantes & van Lier, 2007; Fu & Viraraghavan, 2001; Kornaros & Lyberatos, 2006), coagulation and flocculation (Choi, Shin, Lee, Joo & Lee, 2001; Daneshvar, Sorkhabi & Kasiri, 2004; Golob, Vinder & Simonic, 2005), and membrane processes (Benytez, Acero & Leal, 2006; Suksaroj, Heran, Allegre & Persin, 2005).

Adsorption and chemical treatment processes have shown promise as a practical and economic process for treatment of textile waste; especially for color removal. The advantages of adsorption process are for its simplicity in operation and inexpensive if compared to other separation processes). The most commonly used adsorbent in industrial wastewater treatment systems is activated carbon because it has a large specific surface area, even though it is a bit expensive to run such systems (Sanghi & Bhattacharya, 2006; Shen, Fan, Zhou, Gao, Yue & Kang, 2009). However, there problems are associated with the use of carbon for the adsorption of pollutants: its relatively high cost, regeneration and reuse are difficult, and it is limited to the removal of non-polar materials (Oke, Olarinoye & Adewusi, 2008). Therefore, there is a need to find effective materials for dyes wastewater treatment. Previous studies indicated that many materials such as phyrophyllite (Amran & Zulfikar, 2010), rice husk (Han, Ding, Xu, Zou,

Wang, Li & Zou, 2008), montmorillonite (Gemeay, 2002; Wang & Wang, 2008), plant (Patil & Shrivastava, 2010), bagasse (Ko, Tsang, Porter & McKay, 2003; Zhang, Moghaddam, O'Hara & Doherty, 2011), fungi (Binupriya, Sathishkumar, Swaminathan, Ku & Yun, 2008), soil (Smaranda, Gavrilescu & Bulgariu, 2011), clay mineral (Alpat, Ozbayrak, Alpat & Akcay, 2008; Chen & Zhao, 2009; Dogan, Ozdemir & Alkan, 2007; Hu & Qiao, 2006; Mumin, Khan, Akhter & Uddin, 2007; Ozacar & Sengil, 2004; Shen, Fan, Zhou, Gao, Yue & Kang, 2009; Toor & Jin, 2012; Vimonses, Lei, Jin, Chow & Saint, 2009), fruit shell (Reddy, 2006), water hyacinth root (Rajamohan, 2009), activated carbon (Jayaraj, Thanaraj, Natarajan & Prasath, 2011; Khaled, El-Nemr, El-Sikaily & Abdelwahab, 2009; McKay, 1983), chitosan (Annadurai, Ling & Lee, 2008; Chatterjee, Chatterjee & Woo, 2011), and other adsorbents (Ahmad & Kumar, 2010; Aravindhan, Fathima, Rao &Nair, 2007; Chatterjee, Lee, Lee & Woo, 2009; Chatterjee, Lee & Woo, 2010; Dizge, Aydiner, Demirbas, Kobya, Kara, 2008; Elkady, Ibrahim & Abd El-Latif, 2011; Han, Ding, Xu, Zou, Wang, Li & Zou, 2008; Hou, Zhou, Wu & Wu, 2012; Zulfikar & Setiyanto, 2013; Zulfikar, Setiyanto, Rusnadi & Solakhudin, 2015) had been used and investigated for removal and adsorption of dyes from aqueous solution.

Molecular imprinting technique (MIT) is to use the polymerization between template molecule and functional monomer to prepare molecularly imprinted polymer (MIP) with specific binding sites which can identify template molecule, and these sites are complementary with template molecule in the shape and spatial structure (Castro, Whitcombe, Vulfson, Vazquez-Duhalt & Bárzana, 2001; Rajkumar, Katterle, Warsinke, Möhwald & Scheller, 2008). MIP has been applied to many fields and achieved some promising results (Yang, Liu, Guo, Li, Liu & Xu, 2011; Aburto & S. Le Borgne, 2004; Yang, Liu, Zhou, Xu, Zhou & Huang, 2012; He, Lv, Zhu & Lu, 2010; Yao, Li & Qin, 2008; Zhao, Sheng, Zhu, Wei, Cai, Zhai, Du & Hu, 2010; Zulfikar, Wahyuningrum, Mukti & Setiyanto, 2016).

In this study, the effects of dye initial HA concentration on the adsorption ability of MIP as an adsorbent from aqueous solutions was examined. Both pseudo first and second order adsorption kinetics were applied to the experimental results and kinetic parameters were also calculated.

## 2. Materials and Method

### 2.1 Materials

MIP which were prepared with methyl methacrylate (MMA) as a monomer, methylene blue (MB) as templates and ethylene glycoldimethacrylate (EGDMA) as a cross-linker was obtained from Analytical Chemistry Laboratory, Department of Chemistry, Institut Teknologi Bandung, Indonesia. Metylene blue, C.I. 52015 (MB) was purchased from Merck. Hydrochloric acid used to adjust pH was purchased from Merck. Water used was generated from aqua demineralization system. All materials were used without further purification. Before mixing the MB sample with adsorbent, its pH value was adjusted and measured using 300 Hanna Instrument pH meter.

### 2.2 Method

Adsorption experiments were carried out by agitating 200 mg of adsorbent with 50 ml of dye solution of the desired concentration (50-200 mg/L) and pH 7 at 200 rpm, 25 $^{o}$C in a thermostated rotary shaker (ORBITEK, Chennai, India) for 2, 5, 10, 15, 20, 30, 40, 60, 80, 100, 120 and 180 minutes. Dye concentration was estimated spectrophotometrically by monitoring the absorbance at 663 nm by using a UV-vis spectrophotometer (Shimadzu UV-Vis 1601

model). pH was measured by using a pH meter (300 Hanna Instrument). The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 20,000 rpm for 20 min. The absorbance of supernatant solution was measured. Duplicate samples were measured, and the average was used in subsequent analysis.

The percent of MB adsorption was calculated by using the following equation:

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \text{x } 100\% \quad (1)$$

where $C_i$ and $C_e$ are initial and final concentration (mg/L) of MB in solution, respectively. The adsorption capacity of an adsorbent at equilibrium with solution volume $V$ was calculated using the following equation:

$$q_e \text{ (mg.g}^{-1}) = \frac{C_i - C_e}{m} \text{x V} \quad (2)$$

where $C_i$ and $C_e$ are the initial and final concentration (mg/L) of MB in solution, respectively. $V$ is the volume of solution (L) and $m$ is mass of adsorbent (g) used.

## 3. Results and Discussion

### 3.1 Effect of agitation time and initial concentration dye on adsorption

Generally, the adsorption of MB by MIP showed two stages: a rapid adsorption stage of the first 75 min and a slower stage of 75-200 min (Figure 1). At the start of the adsorption, MB removal can be rapid surface adsorption (external surface adsorption).In the later slower stage, adsorption mainly occurred via transportation of surface-adsorbed dye to the internal adsorption sites of the adsorbent (internal surface adsorption) (Ahmad & Kumar, 2010; Hou, Zhou, Wu & Wu, 2012). Meanwhile, part of external sites were released and cycled for next adsorption. After 75 min, the adsorption reached equilibrium. The adsorption curves are single, smooth and continuous leading to saturation.

From Figure 1, we could also see that the adsorption of dyes depends on the initial concentration of the dye. The percentage of MB adsorption at equilibrium decreased as the MB concentration was increased. This is because an increase in the initial concentration provides an important driving force to overcome all resistances of the dye between the aqueous and solid phases (Elkady, Ibrahim & Abd El-Latif, 2011; Toor & Jin, 2012; Zulfikar & Setiyanto, 2013; Zulfikar, Wahyuningrum & Lestari, 2013; Zulfikar, M.A., Setiyanto, H., Rusnadi, & Solakhudin, 2015). At lower concentrations, all sorbate ions present in the sorption medium could interact with the binding sites, hence higher percentage adsorption results. At higher concentrations, because of the saturation of the sorption sites, the percentage adsorption of the dye shows a decreasing trend (Aravindhan, Fathima, Rao & Nair, 2007; Elkady, Ibrahim & Abd El-Latif, 2011; Toor & Jin, 2012; Zulfikar & Setiyanto, 2013; Zulfikar, Wahyuningrum & Lestari, 2013; Zulfikar, M.A., Setiyanto, H., Rusnadi, & Solakhudin, 2015).

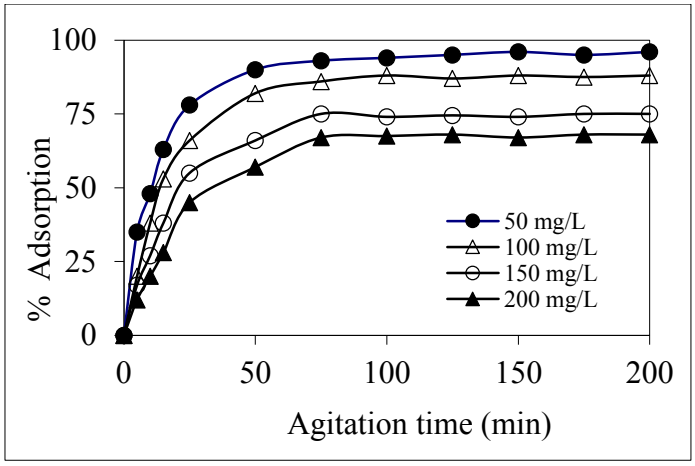


Figure 2. Effect of agitation time and dye concentration on MB adsorption using MIP

### 3.2 Kinetics adsorption

Adsorption kinetics is used to predict the rate at which dye is removed from the aqueous solutions. Several kinetic models including pseudo-first-order, pseudo-second-order and intra-particle diffusion are available to understand the behavior of the adsorbate adsorbed by the adsorbent and to determine the controlling mechanism of the adsorption process. The pseudo first-order model is one of the most widely used equations to describe the adsorption rate based on the adsorption capacity. The linear form is formulated as:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (3)$$

where $k_1$ is the adsorption rate constant ($min^{-1}$), $q_e$ and $q_t$ are the amounts of MB adsorbed at equilibrium and at time $t$(min). The values of $k_1$ and $q_e$ (Table 1) were evaluated from the linear regression of log ($q_e$-$q_t$) versus $t$ (Figure 2). The determination of coefficient value for the pseudo-first-order adsorption model ($R^2$) was very high and close to unity.

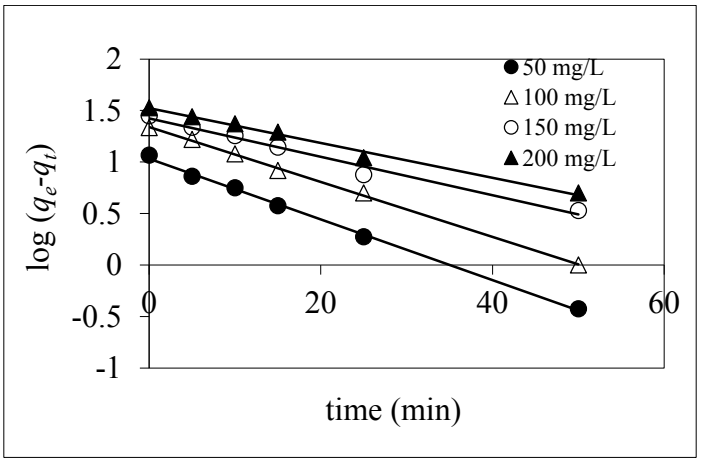


Figure 2. Pseudo-first-order plots for adsorption of MB using MIP

The pseudo-second order model is based on the adsorption capacity of the dye molecules on the surface of the adsorbent and its linear form is expressed as follows:

$$t/q_t = 1/k_2.q_e^2 + t/q_e \quad (4)$$

where $k_2$ (g/(mg min$^{-1}$)) is the constant rate of pseudo-second-order adsorption. The values of $k_2$ and $q_e$ (Table 1) were calculated from the slope and intercept of straight portion of the linear plots obtained by plotting $t/q_t$ against $t$ (Figure 3). It was reported that if adsorption data followed the pseudo-second order model, the overall rate of the dye adsorption process was controlled by the chemisorption process.

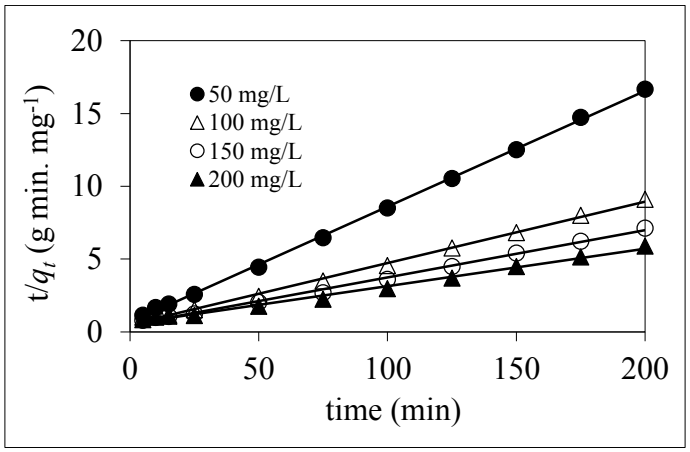


Figure 3. Pseudo-second-order plots for adsorption of MB using MIP

The results in Table 1 showed that the determination coefficient for the second order kinetic model was low and the calculated equilibrium adsorption capacity $q_e$ had a large deviation compared with the experimental data. It suggested that the pseudo-second-order model was not suitable to describe the adsorption of MB onto MIP and the rate-limiting step was not chemisorption.

Table 2. Pseudo-fist and pseudo second order kinetics parameters for MB adsorption

| Dye Concentrations | Pseudo-first-order | | | Pseudo-second-order | | | |
|---|---|---|---|---|---|---|---|
| (mg/L) | $k_1$ (min$^{-1}$) | $q_e$, cal (mg/g) | $R^2$ | $k_2$ (g/(mgmin$^{-1}$)) | $q_e$, cal (mg/g) | $R^2$ | $q_e$, exp (mg/g) |
| 50 | 0.067 | 10.74 | 0.998 | 9.67 x 10$^{-3}$ | 12.66 | 0.999 | 11.63 |
| 100 | 0.060 | 21.88 | 0.998 | 3.49 x 10$^{-3}$ | 23.81 | 0.997 | 21.50 |
| 150 | 0.041 | 26.61 | 0.984 | 2.11 x 10$^{-3}$ | 31.25 | 0.996 | 28.13 |
| 200 | 0.037 | 33.34 | 0.990 | 1,11 x 10$^{-3}$ | 40.00 | 0.993 | 33.50 |

Adsorption is a multi-step process involving transport of the adsorbate (dye) molecules from the aqueous phase to the surface of the solid (MIP) particles then followed by diffusion of the solute molecules into the pore interiors. If the experiment was a batch system with rapid stirring, there was a possibility that the transport of sorbate from solution into pores (bulk) of

the adsorbent is therate-controlling step (Khaled, El-Nemr, El-Sikaily & Abdelwahab, 2009; McKay, 1983). This possibility was tested in terms of a graphical relationship between the amount of dye adsorbed and the square root of time. Since the MB was probably transported from its aqueous solution to the MIP by intra-particle diffusion, the intra-particle diffusion was another kinetic model that should be used to study the rate-limiting step for MB adsorption onto MIP. The intra-particular diffusion is commonly expressed by the following equation:

$$q_t = k.t^{0.5} + c \quad (5)$$

where $k$ and $c$ are an intra-particle diffusion rate constant (mg/g.min$^{0.5}$) and a constant, respectively. The $k$ is obtained from the slope of linier plot of $q_t$vs. $t^{0.5}$. The values of $q_t$ were found to give two lines part with values of $t^{1/2}$ (Figure 4) and the rate constant $k$ directly evaluated from the slope of the second regression line and the values of intercept $C$, which is related to the thickness of the boundary layer.

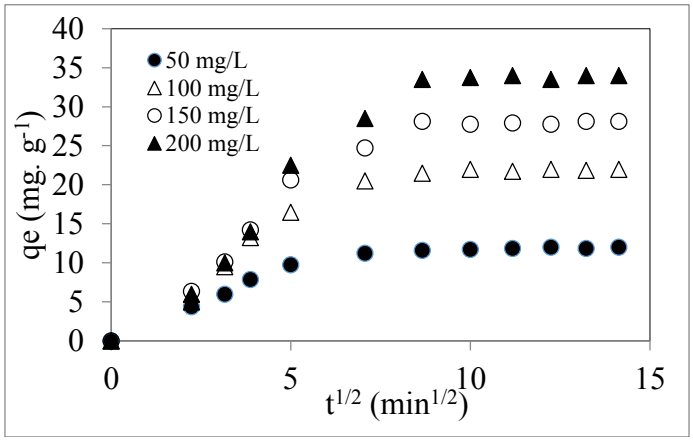


Figure 4. Intra-particle diffusion model plot for the adsorption of MB onto MIP

The shape of Figure4 confirmed that adsorption of the MB onto the MIP was independent of one another, as plot usually showed two intersecting lines depending on the exact mechanism; the first one of these lines represented surface adsorption at the beginning of the reaction and the second one was the intra-particle diffusion at the end of the reaction. As there was still no sufficient indication about which of the two steps was the rate-limiting step. Ho (2003) had shown that if the intra-particle diffusion was the sole rate-limiting step, it was essential for the $qt$ versus $t^{1/2}$ plots to pass through the origin, which was not the case in Figure 4, it might be concluded that the surface adsorption and intra-particle diffusion were concurrently operating during the MB-MIP interactions.

## 4. Conclusion

The main aim of this study was to investigate the adsorption kinetics of MB adsorption onto MIP as an adsorbent. The results from this work showed that the dye initial concentration had an important role in the adsorption of MB onto MIP. The kinetic study of MB on MIP was investigated by using pseudo-first-order, pseudo-second order and intra-particle diffusion equations. The results indicated that the adsorption kinetics followed the pseudo-first-order rate

with intra-particle diffusion as one of the rate determining steps. This work confirmed that the MIP could be used for the removal of cationic dyes from wastewater.

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