Comprehensive Studies on Methylene Blue Adsorption onto Na-bentonite Clay and its Kinetics, Isotherm and Thermodynamics

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Abstract The main objective of this study was to study adsorption of methylene blue (MB) onto Na-bentonite as adsorbent. Firstly, effects of operating factors including initial MB concentration (100-700 mg/L), pH (2-10), temperature (35-55°C), and contact time (0-240 minutes) on performance of adsorption were studied. It was found that these factors had significant effects on both adsorption capacity and percent removal. The adsorption reached equilibrium in a short period of time. Secondly, kinetic and isotherm and thermodynamic studies were investigated. The results revealed that pseudo-first, pseudo-second order and Langmuir models were able to match experimental data using non-linear curve fitting technique. Also, thermodynamic studies indicated that the process under study was spontaneous and endothermic reaction. Finally, a surrogate model was developed to investigate the combined effects of operating factors and examine the optimal operating condition. The optimal result from model prediction was found at initial concentration of 634 mg/L, temperature of 55°C, and pH of 10 and was in good agreement with experimental data indicating applicability of the surrogate model.

1. Introduction

Dyes have been used in several industries, e.g. textile, paper, leather, food, etc. to color their products [1]. Now, there are more than 100,000 commercial dyes available with total annual production of 0.7 million tons and 5-10% of these dyes are discharged as the industrial effluent [2]. Methylene blue (MB) is an example of dye substances commonly used for dyeing various products, such as wood, silk, and cotton [3]. Although MB can be applied to color various products, it potentially causes eye burn and may result in permanent eye injury. In order to avoid problems concerning wastewater, dyes need to be removed before discharge to the environment. Adsorption is among treatment methods showing the potential outcomes to remove different kinds of color substances [4] and activated carbon has been extensively used as an adsorbent for dye removal from solution because of its great properties for adsorption [5]. However, activated carbon for dye removal is expensive so this limits its use in the large scale process. An alternative low cost material for dye removal has been paid attention [6]. Clay minerals are one of the most widely used adsorbents for the dye removal from aqueous solution because of high specific surface areas, cation exchange capacity and abundance in nature. Na-bentonite is selected as adsorbent in this study because it is cheap, widely available, and shows high potential for removing MB molecules from water. Regarding MB removal using Na-bentonite, the common approach to investigate the effects of operating factors is to vary one factor while keeping others constant. This is inadequate to
describe the interaction effects or the simultaneous effects of two or more operating factors on adsorption capacity and select the optimal operating condition for process operation as the interaction effects can provide better understanding of the relationship between operating factors and the adsorption capacity. The main objective is to investigate the individual and interaction effects of operating factors for MB adsorption onto Na-bentonite including pH, temperature, contact time and initial MB concentration. In addition, the pseudo-first and second order kinetic studies were investigated to determine the adsorption kinetic parameters of MB onto Na-bentonite. Then, the equilibrium information and adsorption thermodynamics would be evaluated.

2. Method

The experiment was divided into 2 parts. Firstly, physical and chemical properties of Na-bentonite were investigated using Brunauer–Emmett–Teller (BET) surface area using the Barret-Joyner-Hanlenda (BJH) method [7], Fourier transformed infrared spectroscopy (FTIR 2000), and X-ray diffraction (XRD, X’ Pert Phillips, X’ Pert 2000). Secondly, the individual and combined effects of operating factors were studied including temperature (308.15-328.15 K), initial MB concentration (200-500 mg/L), contact time (0-120 minutes), and pH (2-10). Initially, the stock solution was prepared by dissolving 1 g of MB in 1000 mL distilled water. After that, the stock solution was diluted by using distilled water to give the appropriate MB concentration. The UV/VIS spectrophotometer (λmax = 615 nm) was then used to determine the MB concentration before and after adsorption through a calibration curve or the relationship between absorbance and the MB concentration. Different operating factors of MB adsorption onto Na-bentonite were then investigated. In order to examine the interaction effects of operating parameters, surrogate-based modeling was employed. It is a mathematical technique used for investigating the relative significance of operating factors. It has been used in several manufacturing industries to improve performance and capability. This approach involves experimental planning and designing to collect and analyze appropriate data. As a result, it leads to a valid and reliable conclusion. To develop the surrogate model, it involves a variation of the factors under study simultaneous at their desired levels. This allows us to obtain large amount of data with a small number of experimental trials. The surrogate model in this study was developed based on polynomial respond surface model (RSM) or polynomial approximation defined as:

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\hat{y}(x) = \beta_0 + \sum_{i=1}^{m} \beta_i x_i + \sum_{i=1}^{m} \beta_{ii} x_i^2 + \sum_{i=1}^{m} \sum_{j=1}^{m} \beta_{ij} x_i x_j
\]

where \(\hat{y}(x)\) is the responses of surrogate models; \(\beta_0, \beta_i, \beta_{ii}\) and \(\beta_{ij}\) are constant, linear, quadratic, and crossproduct coefficients, respectively. \(x_i, x_j\)are independent factors (operating factors).

3. Results and discussion

In the first part regarding the physical and chemical properties of Na-bentonite, the results showed that the specific surface area, pore volume, and average pore size were equal to 77.55 m²/g, 0.1044 cm³/g, and 26.92 nm, respectively. For XRD pattern, the diffraction peaks were found at 2\(\Theta\) = 6.55° and 29.37° corresponding to the \(d_{001}\) spacing of 13.49 Å and 3.04 Å. Also, Na-bentonite was composed of mineral montmorillonite and quartz. This could provide the better understanding of crystal structure in mineral clay and spacing between layer sheets. FTIR analysis showed the functional group found in the adsorbent including Si-O-Si bending, Si-O stretching, C-H bending, H-O-H bending, and O-H stretching. In the second part, the effects of initial dye concentration (200-500 mg/L), temperature (308.15-328.15 K), initial pH (2-10) and contact time (0-240 minutes) on adsorption capacity and MB removal efficiency were investigated. It was found that increasing initial MB concentration led to an increase in the adsorption capacity because the higher initial MB concentration causes higher driving force for the mass transfer between the solution and the adsorbent. The contact time is another important operating factor for the adsorption process in terms of both adsorption capacity and economic aspects.
The adsorption capacity increased significantly at the initial period and decreased slightly until reaching equilibrium within a few minutes. The fast adsorption occurred at the initial period because the adsorption sites are exposed at the initial period and this leads to the higher adsorption rate. Figure 1(a) shows the effect of temperature on the adsorption capacity of MB onto Na-bentonite and it was found that the adsorption capacity slightly changed with increasing temperature. With regard to pH, Figure 1(b) shows the MB removal efficiency at different pH. The MB removal efficiency increased with increasing pH because at the lower pH, the higher amount of excess H\(^+\) possibly competes with MB cations to be adsorbed on the available adsorbent sites. This can consequently reduce the amount of MB cations adsorbed on the adsorbent sites. On the other hand, increasing the pH can decrease the amount of competing H\(^+\), which yields a positive result for the adsorption of MB onto Na-bentonite. The interaction effects of operating factors could be well described using the surrogate-based model with the second degree polynomial equation and the analysis of variance (ANOVA) showed that the R\(^2\) was equal to 0.98. This indicated that the model could explain 98% of data variation and only 2% was not captured by the model. With respect to model validation, it was found that the predicted results from the surrogate-based model were in good agreement with experimental data because the adsorption capacity from model prediction was close to the experimental data. For isotherm studies, the Langmuir isotherm were fitted well with the experimental data as shown in Figure 1(a) with the minimum errors (non-linear chi-square test), \(\chi^2\) of 1.41, 0.32, 0.11, 0.42, and 0.97. The kinetics of MB addition onto Na-bentonite followed both pseudo-first and pseud-second order rates as both models provided good agreement with experimental data with equal errors \(\chi^2\) of 0.01, 0.007, 0.004, 0.002, and 0.006. Regarding thermodynamic studies, the results showed that changes in Gibb’s free energy (\(\Delta G^0\)) were negative [-33.42 to -28.18 kJ/mol] with the corresponding \(\Delta H^0\) and \(\Delta S^0\) of +46.99 kJ/mol and +0.24 kJ/mol K, respectively. This indicated that the adsorption process was spontaneous and endothermic.

![Image](image-url)

Figure 1: (a) Isotherm for the adsorption of MB onto Na-bentonite (b) Effect of pH on MB removal efficiency

4. Conclusion

The results of this study suggested that different operating conditions for MB adsorption, e.g. initial concentration, pH, temperature, and contact time had significant effects on both adsorption capacity and percent removal. For kinetics and isotherm studies, pseudo-first, pseudo-second order and Langmuir isotherm models were in good agreement with measured data. In addition, the results from thermodynamic studies showed that \(\Delta G^0\) was negative but \(\Delta H^0\) and \(\Delta S^0\) were positive indicating that the process under study is spontaneous and endothermic reaction. Another contribution in this work was to
develop the surrogate model to investigate interaction effects of operating factors and determine the optimal condition. The results from model prediction were able to match the experimental data suggesting applicability of the surrogate model.

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