

The adsorption of cationic dye from aqueous solution onto acid-activated andesite

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Abstract

The adsorption of cationic dye (i.e., methylene blue) onto acid-activated andesite in aqueous solution was studied in a batch system with respect to its kinetics as a function of agitation speed, initial adsorbate concentration, pH, and adsorbent mass. It was found that the resulting acid-activated adsorbent possessed a mesoporous structure with BET surface areas at around 60 m²/g. The surface characterization of acid-activated andesite was also performed using the zeta-potential measurements, indicating that the charge sign on the surface of the andesite should be negative in a wide pH range (i.e., 3–11). Furthermore, a simplified kinetic model, pseudo-second-order, was tested to investigate the adsorption behaviors of methylene blue onto the clay samples treated under different process conditions. It was found that the adsorption process could be well described with the model. The adsorption capacity parameter of the model obtained in the present work was significantly in line with the process parameters. © 2007 Elsevier B.V. All rights reserved.

Keywords: Methylene blue; Adsorption; Andesite; Acid activation; Kinetic modeling

1. Introduction

Synthetic organic dyes have been widely used for dyeing of textile fibers such as cotton and polyester. However, these chemical materials often pose certain health hazards and environmental pollution. Colored dye effluents with the appearance of color may interfere with light penetration in the receiving water bodies thereby disturbing the biological processes. Further, the effluents, which may be discharged in industrial effluents from dyestuff manufacturing and textile industries, may exhibit toxic effects toward microbial populations and can be toxic and/or carcinogenic to mammalian animal [1]. Therefore, environmental legislation has imposed stringent effluent limits on the concentrations of dye pollutants as chemical oxygen demand (COD), biochemical oxygen demand (BOD) and/or color. For example, the limits of BOD, COD and true color in the industrial effluents from dyeing/textile industries have been set at 30 mg/L, 100–160 mg/L and 550, respectively, according to

the Effluent Standard in Taiwan [2]. Removal methods of dyes in industrial effluents may be traditionally divided into three main categories: physical, chemical, and biological processes [3,4]. Among them, physical adsorption is generally considered to be the most efficient method for quickly lowering the concentration of dissolved dyes in an effluent [5]. In this regard, activated carbon is the most widely used adsorbent for removal of dyes from the aqueous solution. Despite the prolific use of this adsorbent throughout the water/wastewater treatment and other industrial applications, the removal of organic pollutants by activated carbon adsorption remains an expensive process because the adsorbent is still expensive and has high regeneration cost while exhausted. For these reasons, there is growing interest in using low-cost alternatives to carbon adsorbent [6–8]. By contrast with activated carbon, clay is relatively inexpensive due to its accessibility and abundance. In recent years, clay minerals (e.g. bentonite [9], diatomite [10], fuller's earth [11], kaolinite [12], montmorillonite [13], perlite [14], palygorskite [15], pyrophyllite [16], sepiolite [15,17], zeolite [18,19]) possessing the unique surface and pore properties were extensively evaluated for decoloring liquids.

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Andesite, commercially known as wheat-rice-stone, has become more popular with the commercial advertisement via mass media in recent years because it was claimed to possess some cation-exchange capacity (CEC), suggesting that it can be used in environmental protection and health-related applications such as drinking water purification/softening and odor/tasty absorbing [20]. In Eastern Taiwan, the Coastal Range is abundant in this natural mineral, which was characterized by its distinct large light-colored feldspar phenocrysts embedded in the dark-colored groundmass [21]. By examining its mineralogical compositions regarding X-ray diffraction (XRD), it was further found that the clay mineral was rich in the presence of the expandable vermiculite, or highly charged smectite [20], which should be Fe-rich saponite [21]. Based on its 2:1 type aluminosilicate and cation-exchangeable properties in the smectite/saponite-class clay mineral, these characteristics of andesite make it a potential and powerful adsorbent for adsorption or removal of metal cations [20], and organic cations from aqueous solutions [22]. However, the specific surface area of the clay sample was preliminarily obtained according to the measurement of N₂ adsorption–desorption in the authors' laboratory, showing that its BET surface area was below 5 m²/g.

For the purpose of serving it as an effective decolorizing adsorbent, the clay precursor was processed to increase its porosity by acid activation in the present study because the acid-andesite used for the adsorption of cationic dye in aqueous solutions has been scarcely reported in the literature. A basic dye, methylene blue, was selected as a model compound in this work mainly due to its adsorption as a means of determining the adsorption characterization of porous adsorbent with a potential application in the removal of pollutants from aqueous solution [23]. Also, the water-soluble dye has some industrial applications, which may include the dyeing of silk, leather, paper, wool and cotton, and the production of ink and copying paper [24], as well as the quality control test of concrete and mortar [25]. Although methylene blue is not highly toxic to human being, it can cause eye/skin irritation, and human systemic effects including cyanosis and blood changes [26]. With respect to the adsorption equilibrium and kinetics of methylene blue onto acid-activated andesite, the published information is also limited. The present study aimed at providing one option for utilizing the local clay in the water treatment applications. Thus, the dual objectives of this work were to characterize the chemical/physical properties of acid-activated andesite under the specified conditions, and also to examine the fitness to pseudo-second-order model of the data for analyzing the adsorption kinetics at different agitation rates, initial methylene blue concentrations, clay adsorbent masses and initial pH in aqueous solutions.

2. Methods

2.1. Materials

The cationic dye used as target adsorbate in the present study is methylene blue (i.e., Basic Blue 9, or C.I. 52015) with >95% purity, which was purchased from Katayama Chemical Co. (Japan). Its CAS identification information, chemical for-

mula and molecular weight are 61-73-4, C₁₆H₁₈N₃SCl·4H₂O and 319.89 g/mol, respectively. The andesite sample, which was originally from the Coast Ridge of eastern Taiwan (Taitung, Taiwan), has been crushed and ground by a local stone processor. It was preliminarily tested by the examination of particle size distribution using Mastersizer S (dry type module) laser diffraction particle size analyzer (Malvern Instruments Co., UK), showing that the powder sample possessed an appreciable proportion of fine powder with volume median diameter of about 4.2 μm. The sample was first dried in the oven (105 °C) at least 2 h, and then cooled to room temperature for further activation treatment. Sulfuric acid (H₂SO₄, 96 wt%), which was purchased from Merck Co. (Germany), was selected as acid activator in this study to activate the dried sample for the purpose of creating more fine pores. H₂SO₄ and NaOH were used for adjusting initial pH value in aqueous solutions to obtain the extent of the adsorption capacity of methylene blue onto the acid-activated andesite.

2.2. Preparation of acid-activated andesite

The apparatus and chemical activation method with H₂SO₄ employed in the present work were similar to those for chemical activation of spent diatomite as reported previously [27]. The acid treatment was carried out using a Pyrex glass reactor with boiler-reflux condenser and a magnetic stirrer/hot plate (Model No.: PC-420; Corning Co., USA). The andesite sample (about 10 g) was slowly added to 100 cm³ solutions with H₂SO₄ concentration of 2.0N, stirred and maintained at the solution temperature of 90 °C during the activation period of 0.5 h. Afterward, the sample solution was first cooled to room temperature, then filtered off using centrifugal separator and washed sequentially with de-ionized water three times to remove the ions and other residues. The resulting products were finally dried at 105 °C for 24 h, and stored in the desiccator prior to the physical and chemical characterizations.

2.3. Characterization of acid-activated andesite

The physical properties (incl. BET, external and micropore surface areas, total pore volume and micropore volume, as well as average pore size distribution) of acid-activated andesite were obtained by measuring their nitrogen adsorption–desorption isotherms at –196 °C in a surface area and porosity analyzer (Model No.: ASAP 2020; Micromeritics Co., USA). The measurement of the resulting clay adsorbent was replicated four times for the purpose of determining the accuracy of the analytical method.

The cation-exchanging capacity and zeta-potential of acid-activated andesite were measured to characterize its chemical properties. The former was obtained by using the sodium acetate method (Taiwan EPA, NIEM Method S202.60A). The latter was determined by a Zeta Meter System 3.0 (ZETA-METER Inc., USA) to indicate the charges at the surface of the mineral particle. The data on the zeta-potential versus pH was thus applied to elucidate the effect of pH on adsorption of methylene blue onto the clay adsorbent.

2.4. Adsorption studies

All the experiments of adsorption kinetics were carried out in a ca. 3-dm³ stirred batch adsorption apparatus with four baffles as similarly described in our previous studies [27–29]. All the dye solutions were prepared with de-ionized water. The adsorption uptake of the clay adsorbent has been investigated at 25 °C under the controlled process parameters including agitation speed (i.e., 200, 400, and 600 rpm), initial dye concentration (i.e., 10, 20, 30, and 60 mg dm⁻³), clay mass (i.e., 0.5, 1.0, and 1.5 g), and initial pH (i.e., 3.0, 7.0 and 11.0). The solution sample (about 10 cm³) was taken at specified time up to 1 h and then filtrated with fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS, Inc.). The analysis of dye concentration in the filtrate solution was immediately measured with UV/Visible spectrophotometer (Model: U-2001; Hitachi Co., Japan) at a 661 nm wavelength, at which the maximum absorbency occurred. The amount (q_t , mg g⁻¹) of adsorbed dye on the activated andesite was directly determined by the difference between the initial dye and filtrate dye concentrations at any sampling time (t , min), not corrected with the dye purity. In order to evaluate the statistical significance of data in the kinetic experiments, each experiment point was an average of at least two independent tests under identical adsorption conditions.

3. Results and discussion

3.1. Characterizations of acid-activated andesite

3.1.1. Pore properties of acid-activated andesite

It is well known that the acid activation is a common method for replacing exchangeable K⁺, Na⁺ and Ca²⁺ by H⁺ in the interlamellar space of clay minerals (e.g. montmorillonite) and also leaching out a part of the Al³⁺, Fe³⁺ and Mg²⁺ from the lattice structure, thus making the clay physically more porous. The data in Table 1 indicate the surface areas, pore volumes and average pore diameter of the acid-activated clay. In order to acquire

Table 1
Main physical properties of the acid-activated andesite

Physical property	Value ^a
Surface area	
Single point surface area at $P/P_0 = 0.3$	61.04 ± 1.01 m ² /g
BET surface area	61.81 ± 1.00 m ² /g
Langmuir surface area	95.90 ± 1.86 m ² /g
t -Plot micropore area	15.44 ± 1.19 m ² /g
t -Plot external surface area	46.51 ± 1.82 m ² /g
Pore volume	
Single point adsorption total pore volume of pores less than 120–190 nm diameter at $P/P_0 = 0.99$	0.0498 ± 0.0021 cm ³ /g
t -Plot micropore volume	0.00820 ± 0.00058 cm ³ /g
Pore size	
Adsorption average pore width (4V/A by BET)	3.221 ± 0.102 nm

^a Mean ± standard deviation for four determinations.

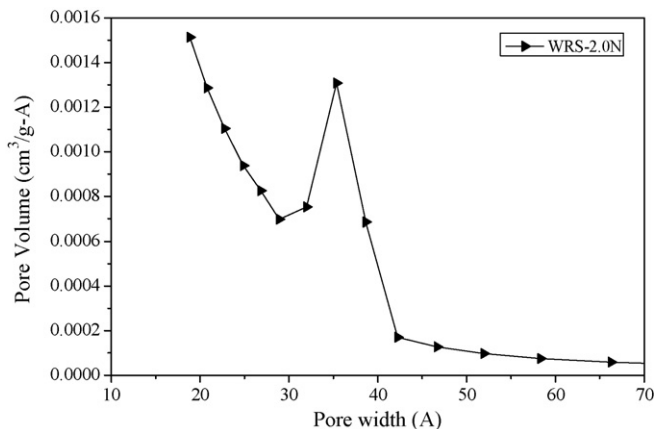


Fig. 1. Plot of pore size distribution of the acid-activated andesite.

the analytical precision and experimental accuracy, these pore properties were obtained from four determinations at a duplicate acid-activated clay, which was carried out under two independent experiments at the same acid activation conditions. From the data in Table 1, it was found that BET surface area and total pore volume of the acid-activated clay adsorbent were moderate, only about 61 m²/g and 0.05 cm³/g (seen in Table 1), respectively. From the nitrogen adsorption/desorption isotherm (not shown), it showed that the clay adsorbent was mainly mesoporous, and was thus characterized by Type IV according to the Brunauer, Deming, Deming and Teller (BDDT) classification [30], which was very similar to those obtained from activated bleaching clay [28]. The mesorosity was consistent with the data on the values of average pore width and the ratio of micropore surface area (or micropore volume) to BET surface area (or total pore volume) in Table 1 and the plot of pore size distribution in Fig. 1. It was also seen in Table 1 that the acid activation experiments conducted in duplicate had high repeatability based on their four pore measurements (i.e., two-pore measurements for each acid-activated sample). On the other hand, the main properties of fresh (untreated) andesite were also determined by the same instrument, giving that its BET surface area and total pore volume are 2.7 m²/g and 0.01 cm³/g, respectively.

3.1.2. Chemical characterization of acid-activated andesite

The surface charges of clay mineral may arise from unequal ionization and dissolution and specific adsorption interactions at the surface because of the presence of ionizable silanol groups (Si–OH) [10,31,32]. Therefore, the hydroxyl group present on the surface of the clay mineral can gain or lose a proton, resulting in a surface charge that is dependent on its pH value in the aqueous solution. Fig. 2 preliminarily showed the zeta-potential of the acid-activated andesite as a function of pH. It was obvious that the surface of acid-activated clay at the experimental conditions (i.e., pH > 3.0) exhibited negative charges mainly due to the variable charge from pH dependent surface hydroxyl sites. These negative charges increase with the increase of the pH while the surface hydroxides lose their protons, and the surface becomes more anionic. This implies that the clay adsorbent may be liable to adsorb molecules

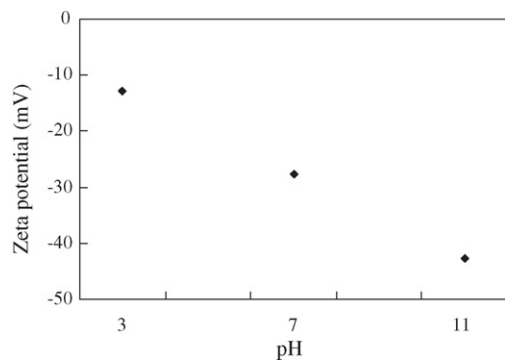


Fig. 2. Plot of ξ -potential vs. pH of the acid-activated andesite.

of cationic dye based on the coulomb interaction. On the other hand, the CEC value of acid-activated andesite was determined by the sodium acetate method (Taiwan EPA, NIEM Method S202.60A) to be about 46.4 meq/100 g. This result was relatively higher as compared to those of common clay minerals such as illite (CEC = 15–40 meq/100 g) [31]. It was also noted that the acid-activated clay on its surface often become negatively charged and was weakly held together by attached exchangeable cations [33], resulting in relatively high in CEC.

3.2. Adsorption kinetics of methylene blue onto acid-activated andesite

The removal of methylene blue (denoted as MB) from the aqueous solution onto the andesite adsorbent was found to be rapid at the initial period of contact time, and then to become slow and even stagnate with the adsorption in progress, implying that an ion-exchange or coulombic interaction between the negatively charged particle surface and methylene blue cation (i.e., MB⁺), a simple kinetic analysis of adsorption, pseudo-second-order equation, was thus used to fit experimental data in the present work [18,34]. Its linear form was commonly expressed as follows:

$$\frac{t}{q_t} = \frac{1}{(kq_e^2)} + \left(\frac{1}{q_e}\right)t \quad (1)$$

where k is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$) and q_e and q_t are the amount (mg g^{-1}) of dye adsorbed at equilibrium and time t , respectively. Rate parameters, k and q_e , can be directly obtained from the intercept and slope of the plot of (t/q_t) against t .

3.2.1. Effect of agitation speed

The effect of agitation speed (i.e., 200, 400, and 600 rpm) on the cationic dye adsorption at the adsorbent mass of 1.0 g, pH of 7.0, and initial dye concentration of 10 mg dm^{-3} was shown in Fig. 3 and also listed in Table 2. Clearly, the correlation between the experimental data and calculated values with the pseudo-second-order model was excellent with the correlation coefficients of higher than 0.99. The results indicated that the residual dye concentration (C_t) or the ratio of residual dye concentration to initial dye concentration (C_t/C_0) was on the gradual decrease as the adsorption time (t) increased. On the

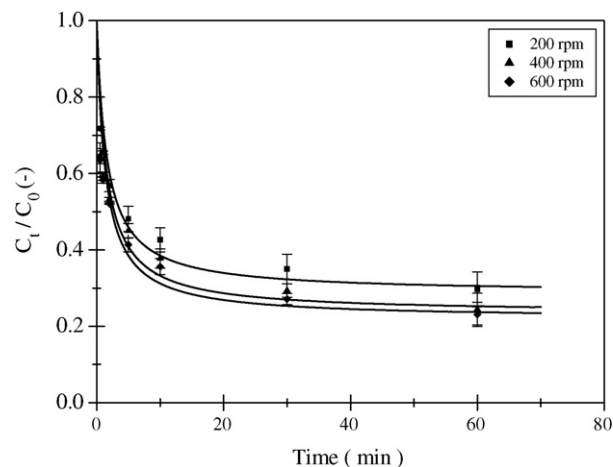


Fig. 3. Plots of adsorbed methylene blue amount vs. time onto the acid-activated andesite at various agitation rates (adsorption conditions: initial methylene blue concentration = 10 mg dm^{-3} , adsorbent mass = 1.0 g, pH 7.0, and temperature = 25°C ; symbols: experimental data, full lines: calculated from pseudo-second-order kinetics model).

other hand, the adsorption capacity (i.e., q_e) was on the increase with agitation speed from 200 to 400 rpm (i.e., 14.3 mg/g versus 15.9 mg/g), but it approached to a plateau as the agitation speed increased from 400 to 600 rpm. This effect can be attributed to the strong turbulence and the very small thickness around the adsorbent particles in the boundary layer as a result of a reduction in the boundary layer resistance and an induction in the mobility of system. For a comparative purpose, with the same dye at the initial concentration of 10 mg dm^{-3} , adsorbent mass of 1.0 g, pH of 7.0, agitation speed of 400 rpm, and temperature of 25°C , the fitting results indicated that the adsorption capacity (i.e., q_e) was only 5.3 mg/g with correlation coefficients (R^2) of over 0.99, which was significantly smaller than that (i.e., 15.9 mg/g) of activated andesite. This is consistent with the measured BET values of 61.0 and $2.7 \text{ m}^2/\text{g}$ for activated andesite and fresh andesite, respectively, described above.

3.2.2. Effect of initial concentration

The effect of initial methylene blue concentration on the adsorption rate of the cationic dye at the adsorbent mass of 1.0 g, pH of 7.0, and agitation speed of 400 rpm was presented in Table 3. As the initial dye concentration increased from 10 to 40 mg dm^{-3} , the adsorption capacity (i.e., q_e) of methylene blue onto the acid-activated andesite increased from 16.0 to 20.0 mg/g , indicating that the initial concentration provided a powerful driving force to overcome the mass transfer resistance

Table 2

Pseudo-second-order parameters for the adsorption of methylene blue onto the acid-activated andesite at various agitation rates

Agitation rate (rpm)	k ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2
200	4.40×10^{-2}	14.3	0.9986
400	4.27×10^{-2}	15.9	0.9988
600	4.68×10^{-2}	15.9	0.9992

Adsorption conditions: initial concentration = 10 mg dm^{-3} , adsorbent mass = 1.0 g, pH 7.0, and temperature = 25°C .

Table 3

Pseudo-second-order parameters for the adsorption of methylene blue onto the acid-activated andesite at various initial concentrations

Initial concentration (mg dm ⁻³)	k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
10	4.27×10^{-2}	16.0	0.9988
20	3.54×10^{-2}	16.4	0.9977
30	4.62×10^{-2}	18.9	0.9990
40	4.80×10^{-2}	20.0	0.9988

Adsorption conditions: adsorbent mass = 1.0 g, agitation rate = 400 rpm, pH 7.0, and temperature = 25 °C.

between the aqueous and solid phases. It was further noted from Fig. 4 that the curves of dimensionless dye concentration versus time were smooth and continuous to saturation adsorption at various initial concentrations of methylene blue on the andesite particles. Again, the kinetic modeling of the dye adsorption onto the andesite adsorbent well followed the pseudo-second-order rate model with the correlation coefficients of higher than 0.998 for all the system in the present work.

3.2.3. Effect of initial pH

The pH is also one of the determining parameters of controlling the adsorption behavior of cationic molecule onto suspended clay particles [28]. In this work, the effect of the three initial pH (i.e., 3.0, 7.0, and 11.0) on the intake rate of methylene blue by the acid-activated andesite was investigated at the adsorbent mass of 1.0 g, agitation speed of 400 rpm, and initial dye concentration of 10 mg dm⁻³. Fig. 5 showed that the ratio (C_t/C_0) of residual dye concentration to initial dye concentration at the pH of 3.0, 7.0, and 11.0 was on the decrease as the adsorption time (t) increased. From the fitting data in Table 4, it was seen that the adsorption capacity (i.e., q_e) of methylene blue onto the acid-activated andesite significantly increased when the pH of dye solution was changed from 3.0 to 7.0. It meant that the charge sign on the surface of the andesite should be negative

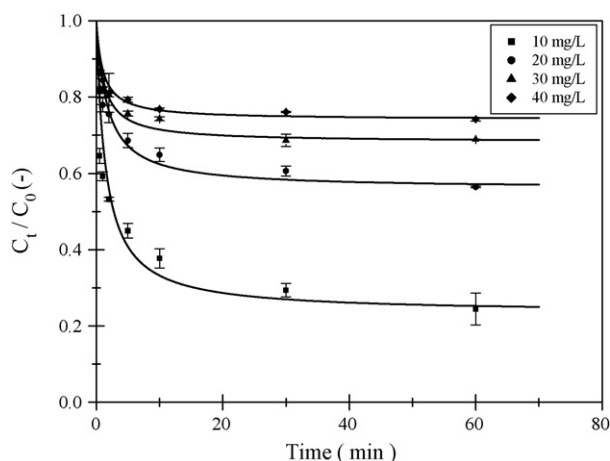


Fig. 4. Plots of adsorbed methylene blue amount vs. time onto the acid-activated andesite at various initial concentrations (adsorption conditions: adsorbent mass = 1.0 g, agitation rate = 400 rpm, pH 7.0, and temperature = 25 °C; symbols: experimental data, full lines: calculated from pseudo-second-order kinetics model).

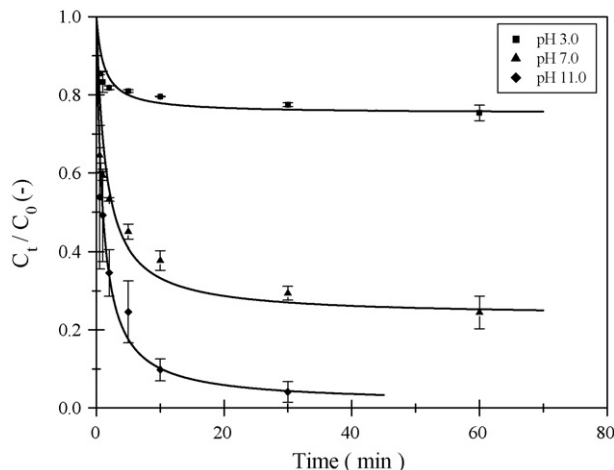


Fig. 5. Plots of adsorbed methylene blue amount vs. time onto the acid-activated andesite at various pH (adsorption conditions: initial methylene blue concentration = 10 mg dm⁻³, adsorbent mass = 1.0 g, agitation rate = 400 rpm, and temperature = 25 °C; symbols: experimental data, full lines: calculated from pseudo-second-order kinetics model).

in a wide pH range (i.e., 3–11), which can also be seen from the data on the zeta-potential (Fig. 2). Therefore, the extent of methylene blue adsorbed on the andesite tended to increase with the increase of pH values, which can be attributed to the electrostatic repulsion between the positively charged surface and the positively charged dye molecule for pH below 7. Also, lower adsorption of MB at acidic pH is due to the presence of excess H⁺ ions competing with dye cations for the adsorption sites. These observations were similar to earlier findings by other workers for adsorption of methylene blue (i.e., basic blue 9) on kaolinite [12] and perlite [14].

3.2.4. Effect of adsorbent mass

The effect of varying the andesite mass on methylene blue adsorption at the initial concentration of 10 mg dm⁻³, pH of 7.0, and agitation rate of 400 rpm has been carried out. The values of pseudo-second-order rate parameters for the adsorption system were listed in Table 5. Also shown in Fig. 6, the correlation between the experimental and theoretical results was still good. It was further found that the ratio (C_t/C_0) of residual dye concentration to initial dye concentration gradually decreased as the adsorbent mass increased. This implied that the number of adsorption sites (or total surface area) increased in parallel with the increase of adsorbent mass. However, the adsorption capacity (i.e., q_e) of acid-activated andesite decreased as its mass increased. Such a phenomenon was similar to those of Ho

Table 4

Pseudo-second-order parameters for the adsorption of methylene blue onto the acid-activated andesite at various initial pH

Initial pH	Final pH	k (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
3.0	2.9	1.66×10^{-1}	5.17	0.9979
7.0	6.7	4.27×10^{-2}	15.95	0.9988
11.0	10.9	6.25×10^{-2}	16.10	0.9992

Adsorption conditions: adsorbent mass = 1.0 g, initial concentration = 10 mg dm⁻³, agitation rate = 400 rpm, and temperature = 25 °C.

Table 5

Pseudo-second-order parameters for the adsorption of methylene blue onto the acid-activated andesite at various adsorbent masses

Adsorbent mass (g dm^{-3})	k ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2
0.5	4.32×10^{-2}	17.57	0.9993
1.0	4.27×10^{-2}	15.95	0.9988
1.5	6.98×10^{-2}	12.94	0.9997

Adsorption conditions: initial concentration = 10 mg dm^{-3} , pH 7.0, agitation rate = 400 rpm, and temperature = 25°C .

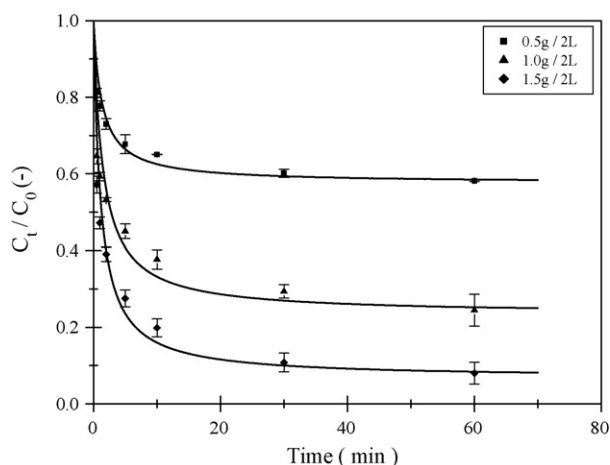


Fig. 6. Plots of adsorbed methylene blue amount vs. time onto the acid-activated andesite at various adsorbent masses (adsorption conditions: initial methylene blue concentration = 10 mg dm^{-3} , agitation rate = 400 rpm, pH 7.0, and temperature = 25°C ; symbols: experimental data, full lines: calculated from pseudo-second-order kinetics model).

and Chiang [34] and Hsu et al. [35] for the adsorption of dye onto activated clay. This was to be reasonably expected because the monolayer coverage of methylene blue on the outer interface of andesite dominated the adsorption system at a fixed dye amount from the time-rate adsorption curves (Figs. 3–6) even if increasing the clay adsorbent mass provided a more surface area and therefore the total number of adsorption sites increased. This would further lead to making a suggestion that higher initial dye concentrations should be tested in conjunction with appropriate adsorbent mass in order to obtain the optimal adsorbent mass.

4. Conclusions

Andesite has proven to be a promising material for the removal of contaminants from aqueous phase. In this work, the BET surface area of resulting acid-activated andesite thus obtained using H_2SO_4 activation method was about $60 \text{ m}^2/\text{g}$, indicating that the porous clay adsorbent was Type IV with hysteresis loop corresponding to the mesoporous structure from nitrogen isotherm measurements. With respect to the suitability of using acid-activated andesite as a mesoporous adsorbent for the adsorption of methylene blue from aqueous solution, the time-adsorption uptake has been examined under various process parameters. The results showed that the adsorption sys-

tem could be explained by the electrostatic repulsion between the positively charged surface and the positively charged dye molecule in the acidic medium, and also attributed to the competitive adsorption of dye cations on the adsorption sites in the presence of excess H^+ ions. Furthermore, the adsorption kinetics of cationic dye onto the clay adsorbent can be well described by pseudo-second-order reaction model. The kinetic parameters thus obtained from the fittings of the model were dependent on agitation speed, initial adsorbate concentration, pH, and adsorbent mass.

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