



# Application of surface modified sericite to remove anionic dye from an aqueous solution

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## ABSTRACT

The treatment of dyeing wastewater is not easy because dyes are mainly aromatic, heterocyclic compounds. The most effective technologies and methods to treat dyeing wastewater are costly and involve materials that are difficult to regenerate after use. Therefore, it is necessary to develop cost-effective, eco-friendly technologies to treat dyeing wastewater. The aim of this study was to investigate the removal of sulfur blue 11 (CI 53235) anionic dye using methyl esterified sericite (ME-sericite) adsorbents in an aqueous solution. The results are discussed in terms of the ME-sericite particle size, temperature, pH value and initial sorption rate according to the initial sulfur blue concentration. In addition, we analyzed the adsorption kinetics using a Pseudo-second-order model with the desorption and reusability. The methyl esterification caused a considerable increase in the specific surface area from 4.45 to 17.62 m<sup>2</sup>/g. The ME-sericite adsorbents successfully removed > 98% of the sulfur dye in the aqueous solution. For the adsorption of 1 mg of sulfur dye, approximately 4.6 to 6.6 g/L ME-sericite were required. The desorption process was carried out by mixing a NaOH eluent to desorb 90.56% of the sulfur dye with 2 h of contact time. Thus, the ME-sericite is a promising adsorbent to treat dyeing wastewater due to its low dose requirement, high removal efficiency and inexpensive material.

**Keywords:** Adsorption, Clay, Dyeing wastewater treatment, ME-sericite, Separation, Sulfur blue

## 1. Introduction

In 2011, world fiber production reached 8,422 million tons, marking an increase by 6.2% when compared to 2010. 71% of the total textile production in the world comes from China (63.6%) and India (7.4%). The textile industry is expected to continue to grow, mainly due to synthetic fibers, and an average annual increase of 3.3% is expected from 8,422 million tons in 2011 to 10,200 million tons by 2020 [1]. Textile dyeing depends the various types of fiber that are used, including vegetable fibers (direct dyes, basic dyes, vat dyes, sulfide dyes and insoluble dyes), animal fiber (basic dyes, acid dyes, mordant dyes and soluble vat dyes) and synthetic fibers (dispersed dyes, insoluble azo dye) [2]. Cellulose, protein, and synthetic fibers are commonly used in the textile industry to produce various textile products [3]. Among those, cellulose fibers are the most frequently used, and sulfur dyes comprise more than 50% of the volume of dyes used for cellulosic fibers [1]. Sulfur dyes are low-cost with good light fastness and are easy to apply.

The textile dyeing industry uses large quantities of water,

producing a large volume of wastewater [4]. Water consumption in the textile dyeing industry increases every year as the fiber production increases, requiring 100-230 L/kg and 150-970 L/kg in 2015 for cotton and wool processes, respectively [5]. Currently, 100-110 million tons of dyestuff are consumed per year around the world, and dyeing wastewater comprises around 2-5% of the various dyestuff, corresponding to about 2-5 million tons [6]. In particular, reactive dyes and sulfur dyes release ca. 20-50% higher dyestuff into wastewater during the dyeing process while basic dyes, disperse dyes and acid dyes release ca. 0-5% into the wastewater [7]. Sulfur blue is inexpensive, has good wash-fastness and is easy to apply. Sulfur blue dyeing is robust against chemical treatments, with the exception of chlorine. Furthermore, this dye is prepared via aqueous sulfuration of *p*-(2,4-dinitroaniline) phenol [1]. In this study, the water-soluble form of sulfur blue was produced through an alkaline reduction with sodium sulfide. Sulfur blue is highly stable in the body, and if ingested, it resists the acidic environment and hydrolytic enzymes of the stomach [1, 8]. Therefore, effluent containing sulfur blue must be washed prior to release into the environment.



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It is not easy to treat dyeing wastewater because dyes are mainly aromatic, heterocyclic compounds. The structure of the dyes is complex, and these are stable and not biodegradable in solution [9]. Thus, the most effective methods and technologies to treat dyes are based on adsorption onto activated carbon. However, this process is costly, and the materials are difficult to regenerate after use [10]. Therefore, developing a cost-effective, eco-friendly technology to treat textile dyeing wastewater is necessary.

Sericite ( $\text{KSi}_3\text{Al}_3\text{O}_{10}(\text{OH})_2$ ) is an abundant clay mineral in soil. It is inexpensive, and its surface hydroxyl groups facilitate the removal of various pollutants. The main components of sericite are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Sericite is closely related to micas, a silicate mineral, and it is easily changed via diagenetic or hydrothermal processes from one to another [11]. The crystalline clay mineral is fine, and the hydrous silicate has a layered lattice structure. The binding of inorganic substances to clays usually takes place through several mechanisms involving physico-chemical adsorption and chemisorption [12]. In general, the surface of natural clay is negatively charged. Therefore, the adsorption rates of anionic dye using natural clays are significantly lower than that for cationic dye adsorption.

To overcome this problem, many researchers have modified natural clay to change its surface charge. In this study, natural sericite was esterified with methylene (ME-sericite), and the negative surface charge changed to positive to adsorb negatively charged sulfur dyes. The binding of sulfur dyes and ME-sericite occurs via physico-chemical adsorption. The ME-sericite has several advantages as an adsorbent, including low cost, non-toxicity, high abundance, and high adsorption capacity for heavy metals and pollutants. Various methods to treat textile dyeing wastewater have been reported [1, 13, 14]. However, ME-sericite has not yet been examined to remove sulfur dye in aqueous solution. Therefore, the aim of this study is to propose the effective use of ME-sericite to remove sulfur dye from an aqueous solution. The objectives are to test the pseudo-second order model to analyze the adsorption of a sulfur dye onto ME-sericite and to assess the usefulness and accuracy of the model. The adsorption kinetics are studied to determine the factors that have an influence, including the particle size of the modified sericite, temperature, pH, and initial dye concentration. A rate parameter ( $k$ ) is defined and used to describe the adsorption of sulfur dye onto the ME-sericite.

## 2. Materials and Methods

### 2.1. Clay Adsorbents

Sericite (Keumnam deposit, Samcheok City, Korea) was used as a clay adsorbent. Sericite contains various metal oxides and minerals, and the chemical composition of sericite is given in the literature [15, 16]. To provide a suitable surface to remove the anionic dye, sericite powder was dried for 24 h at 70°C in order to remove the moisture from the sericite. 2 g of dried sericite powder were treated with 200 mL of 2 mol HCl (Duksan, Korea) containing 2% (v/v) methanol in a 500 mL Erlenmeyer flask, and the mixture

was then shaken for 12 h at 120 rpm at 70°C using a horizontal shaker. After shaking, the mixed solution was centrifuged at 2,000 rpm (645 g), and the supernatant was discarded. The above-mentioned treatment was repeated three times to activate the sericite. The ME-sericite that was produced was rinsed three times with distilled water, dried at 70°C for 24 h in an oven, and stored in a desiccator for future use.

### 2.2. Adsorbate

Clay adsorption was investigated using the anionic dye sulfur blue 11 (CI 53235, molecular weight 305 g/mol, Tera Pharmaceuticals Inc., Buena Park, USA). Sulfur blue is the most commonly used dye in cotton manufacturing [17].

### 2.3. Experimental Design

The sulfur dye removal onto the ME-sericite was investigated according to various parameters, including particle size, pH, temperature, and initial dye concentration. The experiment was carried out as a batch test. The effect of the ME-sericite on the sulfur dye removal was assessed with a ME-sericite particle size of 20 to 100  $\mu\text{m}$ , initial sulfur dye concentration 1 to 40 mg/L, and ME-sericite doses ranging from 1 to 40 mg/L in various concentrations of sulfur dye in 2 L water. In addition, the desorption and reuseability of the ME-sericite was evaluated with NaOH and HCl in a range of 0.05 to 0.2 mol/L. The suspension was shaken for various lengths of time (1 to 120 min) with controlled pH. The pH was controlled from 1 to 12 using NaOH and/or  $\text{H}_2\text{SO}_4$ , and the temperature range from 283 to 313 K was used to assess the effect of the temperature. All experiments were carried out by changing one parameter at a time while holding the others constant. All experiments were repeated five times, and the average results are presented.

### 2.4. Analytical Methods

The Brunauer-Emmett-Teller (BET) surface area and Fourier transform-infrared spectrometry (FT-IR) of the samples were determined using a Protech Korea BET surface area analyzer (Model ASAP 2020) and a FTIR spectroscope (FTIR-2000, Bruker, USA), respectively. The particle size and the amount of sericite were analyzed using laser diffraction (Laser Diffraction Master Class 3&4, Malvern, UK) and micro scales (XP26, Mettler Toledo, Switzerland), respectively. The zeta potential measurements of the sericite and ME-sericite in aqueous solution were conducted using a Malvern Zetasizer Nano-Z analyzer.

Definite amounts of ME-sericite were added to aqueous solutions of sulfur blue, followed by shaking with a variation in time and temperature. The suspension was then centrifuged at 2,300 rpm for 20 min, and the supernatant was removed from the middle of the dye suspension at various time points. The remaining suspension was filtered with a 0.45  $\mu\text{m}$  membrane filter (Whatman, Sigma-Aldrich) to separate the filtrate and the residue. The filtered samples were then measured at a peak wavelength of the dye ( $\lambda_{\text{max}}$  sulfur blue = 620 nm) using a UV-2550 UV-vis spectrophotometer (Shimadzu, Japan). The adsorption capacity was then calculated using the following equation:

$$q_e = \{(C_o - C_e)V\}/m \quad (1)$$

where  $q_e$  (mg/g) is the adsorption capacity, the dye taken up by a unit weight of adsorbent,  $C_o$  (mg/L) is the initial concentration of dye,  $C_e$  (mg/L) is the residual concentration of dye,  $V$  (L) is the volume of the solution, and  $m$ (g) is the weight of the adsorbent.

The dye removal efficiency (%) was calculated as follows:

$$R = \{(C_o - C_e)/C_o\} \times 100\% \quad (2)$$

where  $R$  (%) is the removal efficiency,  $C_o$  (mg/L) is the initial concentration of the dye, and  $C_e$  (mg/L) is the residual concentration of the dye.

A linear equation is obtained for the pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3)$$

$$h = kq_e^2 \quad (4)$$

where  $q_e$  is the amount of adsorbate adsorbed at the equilibrium (mg/g),  $q_t$  is the amount of adsorbate adsorbed at time  $t$  (mg/g),  $k$  (g/mg·h) is adsorption rate constant of the pseudo-second order model,  $h$  (mg/g·h) is the initial sorption rate, and  $R^2$  is the correlation coefficient for the different dye concentrations calculated from the data in these plots.

### 3. Results and Discussion

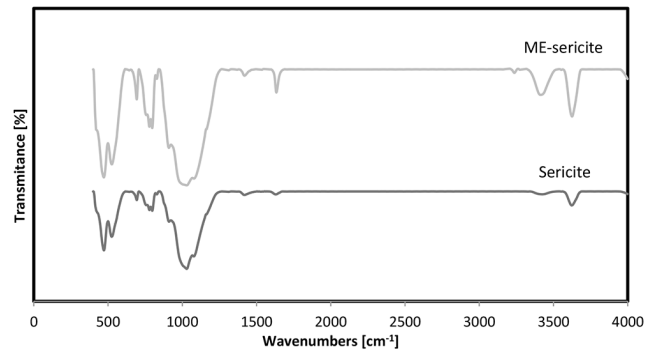
#### 3.1. Characteristics of Natural Sericite and ME-sericite

The BET specific surface area, pore volume, and pore size of sericite and ME-sericite are shown in Table 1. The pore size and pore volume of the sericite increased markedly after methyl esterification. Moreover, this activation resulted in a marked increase in the specific surface area from 4.45 to 17.62 m<sup>2</sup>/g. In recent years, many researchers have expressed interest in increasing the sorption capacity of natural clay. Clay can be modified through various methods, including acid treatment and heat treatment. Özcan et al. [18] modified natural bentonite with Dodecyl-trimethylammonium bromide (DTMA), and the adsorption capacity of DTMA-bentonite was found to be around 11 times higher than that of natural bentonite. Similar results have been found in previous reports. Researchers have also found that after acidification, bentonite, sepiolite and sericite exhibit an increase in adsorption capacity of around 5 to 62 times compared to the natural variants, resulting in a more effective adsorbent for dye treatment in aqueous solutions [11, 19, 20]. In this study, the methyl-esterification of sericite resulted in an increase in the surface area of around 4 times that of natural sericite. This increase in the surface area can contribute to a more effective dye removal.

The adsorbent materials, sericite and ME-sericite, were characterized via FT-IR analysis in the range from 400 to 4,000 cm<sup>-1</sup> (Fig. 1). The absorption spectrum was observed at 3,420 cm<sup>-1</sup>

**Table 1.** Textural Properties of Sericite and ME-sericite

Materials	BET specific surface area (m <sup>2</sup> /g)	Pore size (nm)	Pore volume (cm <sup>3</sup> /g)
Sericite	4.45	3.45	0.069
ME-Sericite	17.62	4.43	0.105



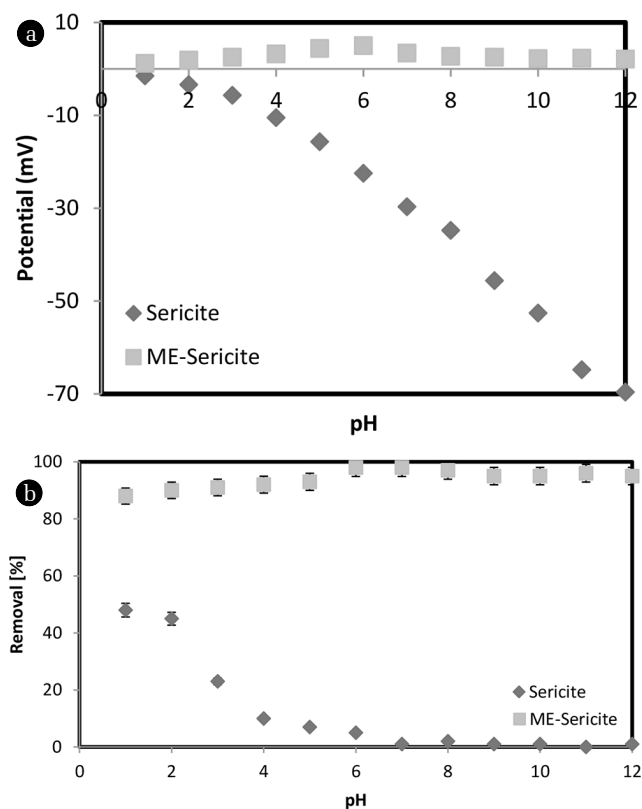
**Fig. 1.** FT-IR spectra obtained for sericite and ME-sericite.

and 3,620 cm<sup>-1</sup> for -OH stretching, confirming the presence of Si-OH, and at 1,670 cm<sup>-1</sup>, which is associated with C = O stretching frequencies. The stretching band at 3,620 cm<sup>-1</sup> was attributed to the presence of the free hydroxyl groups within the layers of the solid sample [11]. The peak obtained at 3,620 cm<sup>-1</sup>, 3,420 cm<sup>-1</sup> and 1,630 cm<sup>-1</sup> significantly increased after methyl esterification of the sericite. Moreover, a frequency band between 900 and 1,300 cm<sup>-1</sup> was assigned to the asymmetric stretching vibrations of C-O-Si, and the size of these peaks increased significantly. The absorption bands at 700 and 800 cm<sup>-1</sup> confirmed the presence of Si-C-H, and the bands observed at 530 and 470 cm<sup>-1</sup> were ascribed to the O-Si-O bending vibrations.

#### 3.2. Parametric Study

##### 3.2.1. Effect of pH

The zeta potential is the potential difference across the phase boundaries between solids and liquids, and it is a measure of the electrical charge of particles suspended in a liquid. Since the zeta potential is not equal to the electric surface potential in a double layer or to the Stern potential, it is often the only value that can be used to describe the double-layer properties of a colloidal dispersion [21, 22]. Fig. 2(a) shows the trend of the potential for sericite and ME-sericite according to the pH. The potential for sericite decreased from -1.5 ± 0.1 mV at pH 1 in control to -69.6 ± 0.6 mV at pH 12 with 30 mg/L of sericite. In contrast, after methyl esterification, the potential of the ME-sericite at 30 mg/L resulted in a positive value, varying from 1 to 5 mV over all pH ranges. In general, zeta-potential values of 0 to ± 5 mV suggest rapid adsorption [21] since sulfur dye adsorption on sericite and ME-sericite is a result of particle collision and charge interaction between the charges of the clay and the dye surface in an aqueous solution. The apparent surface charge of the organic/inorganic matter is represented by its zeta potential, which may affect its adsorption efficiency [22].



**Fig. 2.** (a) Potential of sericite and ME-sericite according to pH ( $C_0$ : 300 mg/L,  $d_p$ : < 35  $\mu\text{m}$ ,  $S$ : 500 rpm (50 min),  $T$ : 283 K and  $m_s$ : 30 mg/L) and (b) Removal of sulfur blue by sericite and ME-sericite according to pH ( $C_0$ : 10 mg/L,  $d_p$ : < 35  $\mu\text{m}$ ,  $S$ : 500 rpm (50 min),  $T$ : 283 K and  $m_s$ : 30 mg/L).

The pH is an important parameter during dye adsorption. The pH of an aqueous solution will control the magnitude of the electrostatic charges that are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous solution [22]. The effect of the pH on the sulfur dye-ME-sericite adsorption process was studied with a fixed ME-sericite dose and sulfur dye concentration in the aqueous solution. The pH was controlled using 0.5 mol/L NaOH and HCl solutions and was then shaken until reaching equilibrium. The removal efficiency of ME-sericite for sulfur blue was determined according to the pH (Fig. 2(b)). The removal efficiency of ME-sericite for sulfur blue was 88-100%, irrespective of pH. The sulfur blue removal efficiency of ME-sericite increased slightly from pH 1.0 to 6.0 and remained almost constant at pH 7.0 to 12.0. Moreover, the sulfur blue removal reached  $\sim 100\%$  at pH > 7.0. In contrast, the removal of sulfur blue with sericite decreased from 48% to 1% as the pH increased from 1.0 to 12.0. At pH > 5.0, the sulfur blue removal decreased significantly and became negligible at pH 7.0 to 12.0. This result was strongly related to the zeta potential of ME-sericite. Various clay minerals, such as kaolinite bentonite, smectite, montmorillonite, etc., have often been used as adsorbents for different dyes. A prior study reported that a cationic dye was adsorbed to around 16 mg/g by kaoline,

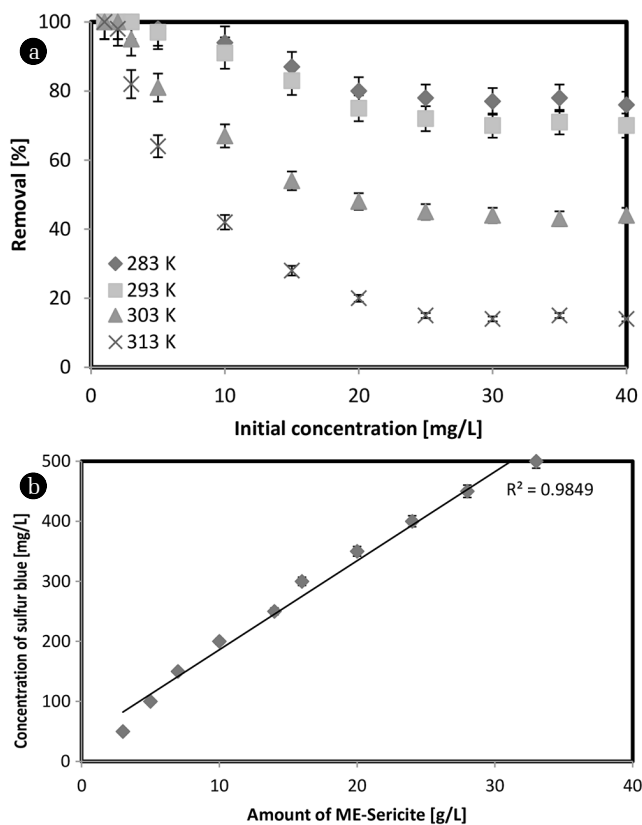
10 mg/g by montmorillonite, and 496.5 mg/g by bentonite. However, an anionic dye was adsorbed at around 2.3 mg/g for kaolinite, 2.6 mg/g for montmorillonite, and 10.5 mg/g for bentonite [1]. This significant difference between cationic and anionic adsorption by natural clays is likely due to the ion exchange capacities. The surface of the clay mineral structure is generally charged to a net negative [14], and the repulsion increased when negatively charged clay particles collide with anionic dye ions. Therefore, the anionic dye adsorption rates for non-modified clays, such as montmorillonite, kaoline and bentonite, are significantly lower than those for cationic dyes. To overcome these problems, sericite was esterified with methylene to change the negatively surface charge to positive. The positively-charged ME-sericite has excellent adsorption for sulfur blue anionic dye.

### 3.2.2. Effect of initial concentration

The initial dye concentration is an important parameter to remove the sulfur dye in an aqueous solution using ME-sericite because it depends significantly on the available binding site of the ME-sericite surface. The optimal initial sorptive concentration was assessed by varying the initial concentration of sulfur blue from 1 to 40 mg/L at pH 7.0. The equilibrium sorption data are shown in Fig. 3(a). The adsorption of sulfur blue on ME-sericite increased from 68 mg/g to 162 mg/g as the initial concentration of the sulfur dye increased from 1 mg/L to 40 mg/L. However, the sulfur dye removal percentage decreased from 100% to 85% as the concentration of the sulfur dye increased from 1 mg/L to 40 mg/L. This may be due to the saturation of adsorption sites on the ME-sericite surface as the initial dye concentration increased. When there is a low concentration in aqueous solution, the active sites of the ME-sericite surface are unoccupied. However, an increase in the initial dye concentration results in a lack of active sites required for the dye molecules [2]. In contrast, the increase in the initial dye concentration will result in an increase in the loading capacity of ME-sericite, and this may be due to the high driving force for the mass transfer at a high initial concentration [23].

### 3.2.3. Effect of the temperature

The effect of the temperature on the sulfur dye adsorption process can be carried out by preparing the sulfur dye-ME-sericite solution at a different initial concentration and then shaking until reaching equilibrium at 283, 293, 303 and 313 K. The temperature is another factor that is important during adsorption because it is an indicator of whether the process is endothermic or exothermic. Adsorption is exothermic when the adsorption capacity decreases as the temperature increases, and this may be due to the increasing temperature lowering the adsorptive forces between the dye molecules and the active sites on the adsorbent surface as a result of a decreased capacity for adsorption. In contrast, the adsorption capacity increases as the temperatures increases when adsorption is an endothermic process. This may be indicative of the increase in the mobility of the dye molecules and in the number of active sites on the adsorbent as the temperature increases [2]. This effect mainly depends on the movement of the dye molecules of each dye class. In this study, sulfur blue removal was significantly dependent on temperature. The adsorption of sulfur blue on ME-sericite decreased from 145 mg/g to 64 mg/g as the initial



**Fig. 3.** (a) Effect of the initial concentration and temperature on sulfur blue removal ( $d_p$ :  $< 35 \mu\text{m}$ , pH: 7, S: 500 rpm (50 min), and ms: 30 mg/L) and (b) Adsorbent dosage effect on the adsorption capacity ( $d_p$ :  $< 35 \mu\text{m}$ , S: 500 rpm (50 min), T: 283 K and removal rate  $> 98\%$ ).

temperature increased from 283 K to 313 K, whereas the removal percentage of sulfur blue decreased to  $\sim 76\%$ ,  $\sim 70\%$ ,  $\sim 44\%$  and  $\sim 14\%$  as the temperature increased to 283, 293, 303 and 313 K, respectively (Fig. 3(a)). These results indicate that the sorption of sulfur blue onto ME-sericite is exothermic.

#### 3.2.4. Effect of ME-sericite dose

The adsorbent dose is also as important as the initial concentration and temperature in the adsorption process because it has a significant effect on the adsorption capacity of the adsorption process [24]. The relationship between the concentration of sulfur blue and the amount of ME-sericite was investigated using  $< 35 \mu\text{m}$  particles at pH 7 (Fig. 3(b)). The correlation coefficient for the sulfur blue concentration and ME-sericite mass was  $> 0.98$ . Approximately 4.6 to 6.6 g/L of ME-sericite were required for the adsorption of 1 mg of sulfur blue. ME-sericite was more effective in removing sulfur blue than other clays. Kaoline removed 24% of sulfur blue anionic dye [17], and montmorillonite removed 27% [25]. However, activated carbon and activated carbon fiber are more effective than natural clay. High removal rates ( $> 90\%$ ) of cationic, mordant and acid dyes have been achieved using activated carbon. The sulfur dye removal was 40.8%, and it increased with the use of massive quantities of activated carbon

( $> 30 \text{ g/L}$  to remove 1 mg/L sulfur blue) [26]. Shen et al. [27] reported that  $> 95\%$  of the dye was removed using ACF at an initial sulfur dye concentration of 60 mg/L. ACF has a higher adsorption capacity, higher surface area ( $1,000 \text{ m}^2/\text{g}$ ), faster adsorption and desorption rates and is easier to manufacture than conventional activated carbon [1]. However, the processing costs of ACF are higher than those for other types of activated carbon [1, 28].

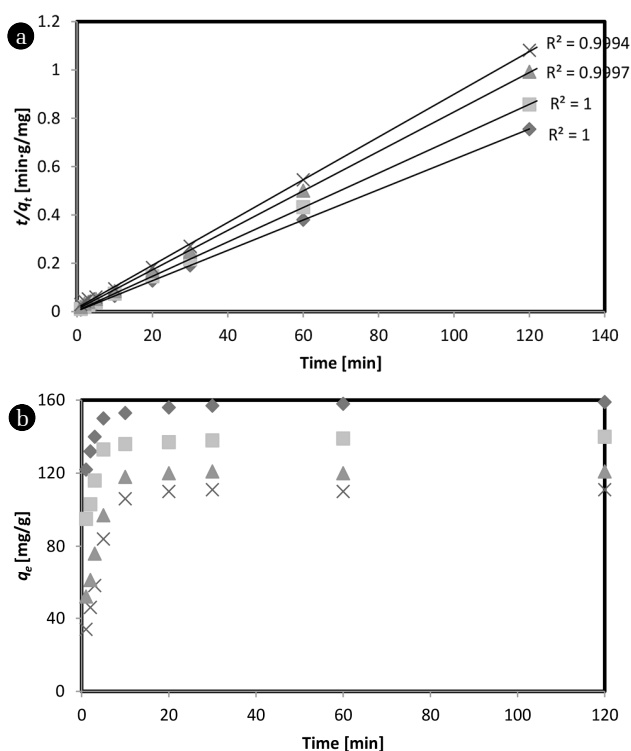
### 3.3. Adsorption Kinetics

A fast absorption rate and a large absorption capacity are important to choose a material that is a better absorbent. The adsorption dynamics can be studied according to the kinetics of adsorption in terms of the order of the rate constant [24]. In this study a pseudo-second-order model was used to analyze the adsorption kinetics. The pseudo-second-order equation that was used is based on the sorption capacity of the solid phase, with the pseudo-second-order model assuming that chemisorption may be the rate-controlling step during adsorption [2].

Linear plots for  $t/q_t$  by  $t$  in Fig. 4(a) show the applicability of the pseudo-second order equation for sulfur dye adsorption with ME-sericite particles of  $< 35 \mu\text{m}$  to  $76\text{--}100 \mu\text{m}$ . The linear regression correlation coefficient ( $R^2$ ) values obtained with the pseudo-second order rate were higher than 0.9994 for all systems with 120 min of contact time. Many researchers have evaluated the adsorption of various dyes using low cost materials [29–31] and found that the pseudo-second-order model is a better fit than the pseudo-first-order kinetics, and the values of  $R^2$  for the pseudo-first-order model are between 0.70 and 0.85 while the values of  $R^2$  for the pseudo-second-order model are up to 0.9905.

The influence of the size of the ME-sericite adsorbent particles on sulfur dye adsorption was investigated in the range from 20 to  $100 \mu\text{m}$  with an initial concentration of 160 mg/L at 283 K, 30 mg/L of ME-sericite dose, and pH 7. The maximum removal rates at 120 min were 99.38%, 87.5%, 75.63% and 69.38% for  $< 35 \mu\text{m}$ ,  $36\text{--}60 \mu\text{m}$ ,  $61\text{--}75 \mu\text{m}$  and  $76\text{--}100 \mu\text{m}$ , respectively. The smallest particle size of  $35 \mu\text{m}$  was more effective due to the inverse relationship between the surface area and the particle size. Similarly, Ho et al. [17] reported that the basic red 18 sorption capacity of clay was 157 mg/g for a particle size of  $0\text{--}38 \mu\text{m}$  and 110 mg/g for  $75\text{--}106 \mu\text{m}$ . In this study, the specific surface area of ME-sericite, dye removal capacity and initial sorption rate increased as the ME-sericite particle size decreased for a given mass of activated clay. This may be due to the fact that the external surface area available for a rapid reaction decreased as the particle sizes increased for an adsorbent with for constant mass. Equilibrium was reached for all samples over a very short time (Fig. 4(b)).

The changes in the parameters according to the particle size are shown in Table 2. The values of  $k$  and  $h$  decreased as the particle size increased. Therefore, reactions involving small ME-sericite particles proceeded more rapidly than those involving larger particles due to their greater external surface area. Moreover, the sorption rate and amount of sulfur dye adsorbed on the ME-sericite decreased as the temperature increased. The temperature is strongly affected by the sorption rates and is reflected by the extremely high correlation coefficients.



**Fig. 4.** (a) Pseudo-second order sulfur blue adsorption kinetics of ME-sericite particles of the following sizes (b) Plot of the sulfur blue adsorption versus time for ME-sericite particles of various sizes: (35  $\mu\text{m}$  (◆), 36-60  $\mu\text{m}$  (■), 61-75  $\mu\text{m}$  (▲) and 76-100  $\mu\text{m}$  (X),  $C_0$ : 160 mg/L, pH: 7, S: 500 rpm (50 min), T: 283 K and ms: 30 mg/L).

**Table 2.** Parameters of the Effect of the Particle Size and Temperature on Sulfur Blue Removal

Particle size	$R^2$	$q_e$	$k$	$h$
< 35 $\mu\text{m}$	1.000	159	5.946	150.32
36-60 $\mu\text{m}$	1.000	140	1.951	38.23
61-75 $\mu\text{m}$	0.998	121	1.457	21.34
76-100 $\mu\text{m}$	0.999	111	0.959	11.81

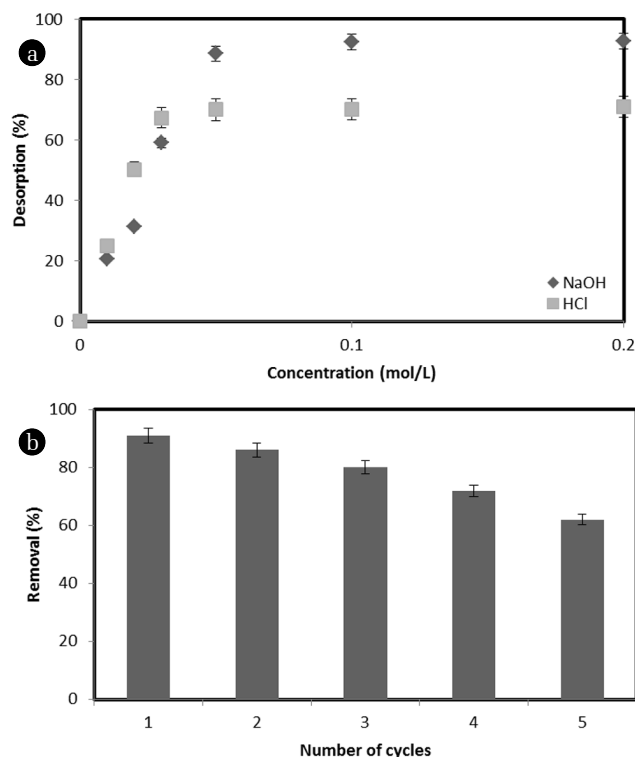
  

Temperature (K)	$R^2$	$q_e$	$k$	$h$
283	1.000	145	1.15	241.78
293	1.000	134	1.23	220.85
303	0.998	96	1.31	120.72
313	0.999	64	1.37	56.11

$C_0$ : 160 mg/L,  $q_e$  (mg/g),  $k$  ( $\times 10^{-3}$  g/mg h),  $h$  (mg/g h)

### 3.4. Desorption and Reusability

The desorption rate is proportional to the driving force, and the desorption kinetics are very important to model the contaminant transport [2]. Moreover, finding a good solvent to reuse the adsorbent



**Fig. 5.** (a) Desorption of sulfur blue from ME-sericite using NaOH and HCl and (b) Percentage removal of sulfur blue in sequential adsorption-desorption cycles.

is important from an economic point of view as is finding of eco-friendly and/or low-cost adsorbents. For the desorption process, the eluent is mixed with dye-saturated ME-sericite, and it is then shaken for a fixed amount of time until the dye is extracted on the eluent. After extraction, the adsorbent is separated using filtration, and the desorbed sulfur dye is measure. The percentage of sulfur dye that is desorbed using various concentration of NaOH or HCl is given in Fig. 5(a). NaOH eluent is more suitable than HCl. The desorption percentage with HCl was higher than that for NaOH at concentrations as low as 0.03 mol/L or less. This suggests that an increase in the OH<sup>-</sup> ion in the aqueous solution with a higher concentration of NaOH increased the repulsion between the OH<sup>-</sup> ion and the anionic sulfur dye. However, at lower concentrations of NaOH (< 0.03 mol/L), the repulsive force is relatively lower than at the higher concentration of NaOH, and thus, desorption is lower than that with HCl eluent. The results indicate that 0.05 mol/L NaOH could desorb 90.56% of sulfur dye within 2 h of contact. The desorption percentage with HCl was lower than that using NaOH, and 69.95% of the sulfur dye is desorbed with 0.05 mol/L HCl. The desorption increased to ~92.75% with 0.2 mol/L NaOH and ~70.92% with 0.2 mol/L HCl for sulfur dye. However, NaOH and HCl concentrations above 0.05 mol/L did not result in a significant increase in the desorption of sulfur dye. Therefore, the 0.05 mol NaOH solution was recommended to regenerate the ME-sericite.

The reusability of the ME-sericite for sulfur dye adsorption with 0.05 mol NaOH is shown in Fig. 5(b). The sulfur dye adsorp-

tion decreased as the adsorption-desorption cycles increased. However, about 62% of the sulfur dye was adsorbed even after the material had passed through five adsorption-desorption cycles. Therefore, the results of this study indicate that ME-sericite is a suitable, excellent material for multiple uses of sulfur dye adsorption from aqueous solution.

Various dye removal methods, including using activated carbon [26], biological methods [32-34], coagulation/flocculation methods [35] and electrochemical methods [13, 36], have been successfully used to treat dyeing wastewater. However, several of these methods have important limitations, including being energy-intensive, expensive, and having a low removal efficiency [1, 9]. Recently, activated carbon fiber (ACF) has emerged as an adsorbent for dye and heavy metal removal [26]. However, the processing cost is an important factor for the use of adsorbents, and ACF generally has low physical strength and is costly at \$195-236 USD per kilogram [13]. In contrast, ME-sericite is inexpensive (\$0.06-0.19 USD per kilogram) [15]. Therefore, the removal method proposed in this study can reduce the cost of treating dyeing wastewater.

## 4. Conclusions

Natural sericite was modified with HCl containing 2% (v/v) methanol for 10 h at 80°C to provide a suitable surface for anionic dye removal. After methyl esterification, the specific surface area of sericite significantly increased, and the surface charge changed from negative to positive. Moreover, the potential of 30 mg/L of ME-sericite was positive, and it varied from 1 to 5 mV for all pH ranges. Thus, the negatively charged sulfur dye was quickly adsorbed by the positively charged ME-sericite. ME-sericite successfully removed > 98% of sulfur blue in an aqueous solution via physicochemical adsorption. The adsorption capacity decreased from 145 to 64 mg/g as the temperature increased from 283 K to 313 K. This means that the adsorption of sulfur dye onto ME-sericite is exothermic. The desorption process with NaOH eluent was indicated to be more suitable than HCl. The results of the adsorption indicated that 0.05 mol/L NaOH could desorb 90.56% of sulfur dye within 2 h. The low dose requirement, high removal efficiency and inexpensive material represent clear advantages of ME-sericite compared to other commonly-used adsorbents.

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