Congo red dye removal from aqueous solution by acid-activated bentonite from sarolangun: kinetic, equilibrium, and thermodynamic studies

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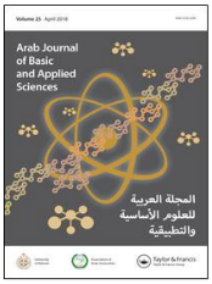

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ORIGINAL ARTICLE

Congo red dye removal from aqueous solution by acid-activated bentonite from sarolangun: kinetic, equilibrium, and thermodynamic studies

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ABSTRACT

The abundant natural bentonite from Sarolangun deposit of Jambi Province, Indonesia, has been successfully activated by a wet acid activation method and applied as a low-cost, and environmental-friendly adsorbent for Congo red dye removal from aqueous solution. The activated bentonite samples were characterized by powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), N_2 adsorption-desorption, and X-ray fluorescence (XRF). The batch adsorption technique has been conducted to study the adsorption behavior of Congo red on activated bentonite. The effects of operational parameters toward the Congo red adsorption on activated bentonite, including adsorbent dosage, initial pH, contact time, initial concentration, and temperature were investigated. Moreover, the properties of adsorption kinetics, adsorption isotherm, and adsorption thermodynamic were also investigated. The results of material characterization showed that acid-activated bentonite has better properties than natural bentonite. For instance, the surface area of acid-activated bentonite elevated almost five-fold compared with natural bentonite. The batch adsorption study showed that the Congo red adsorption on acid-activated bentonite was significantly affected by adsorbent dosage, initial pH, contact time, dye concentration, and temperature. The adsorption kinetics investigation revealed that adsorption was best evaluated by a pseudo-second-order model rather than pseudo-first-order model. The adsorption equilibrium study described that the adsorption process followed the Langmuir isotherm model. The result of thermodynamic investigation revealed that the adsorption process occurred spontaneously and favorably in high-temperature conditions.

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KEYWORDS
Natural bentonite; acid activation; adsorption; Congo red

1. Introduction

As one of many developing countries, growth of the traditional textile industry in Indonesia gradually increased year by year. During the dyeing process in the conventional textile industry, an amount of dye remain which can permeate the fabric and be released to the environment owing to limitations of the wastewater treatment plant (Irmanto & Suyata, 2008). Commonly, dyes used in the textile industry are synthetic with high resistance to oxidizing agents, biodegradation and photodegradation treatment (Wasti & Ali Awan, 2016). Based on the paper reported by Shu et al. (2015), Congo red is one of the most common synthetic dyes used in the textile industry. It is a group of benzidine-based anionic diazo dyes with high toxicity and irritant properties to eye and skin contact. At a high level of contamination, it could induce some respiratory problems and even could be a carcinogenic agent to humans. Consequently, Congo red removal from wastewater of the textile industry is a necessity in order to avoid environmental issues.

In order to remove the dye contamination from wastewater, various technologies have been developed including filtration, coagulation, electrochemical oxidation, chemical oxidation, membrane filtration, adsorption or biosorption, and microbiological treatment (El Haddad, Regti, Slimani, & Lazar, 2014b; Peng, Luan, Chen, Tian, & Jia, 2005; Wang et al., 2016). Among all techniques mentioned, adsorption is considered as the most feasible method to remove the dye contamination in aqueous conditions (El Haddad, Mamouni, Saffaj, & Lazar, 2012). Adsorption is a well-known separation method with high effectivity for water contaminant removal. The adsorption technique currently appears as the most efficient method due to the simplest operation, adsorbent reuse capability, insensitivity to the toxic pollutant, high efficiency and, moreover, low-cost operation (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010).

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Recently, clay and clays mineral have been widely used in broad application fields, i.e. cosmetics, oil mining, pharmaceutical, food, and paper industries. The high demand on the clay's utilization in diverse areas is influenced by its natural abundance, low cost, high cation exchange capacity (CEC), large surface area, and high adsorption capacity. However, natural clays cannot be used as found and need further appropriate modification by chemical or physical methods (Bilgiç et al., 2014).

Bentonite is one of the most utilized clay materials. It is a naturally occurring clay that is mainly constituted of montmorillonite mineral. Bentonite is also well known as dioctahedral 2:1 layer silicate with high swelling properties. The substitution of Mg^{2+} for Al^{3+} in the octahedral structure and Al^{3+} for Si^{4+} in tetrahedral structure causes a permanent negative charge on the bentonite surface. This negative charge commonly equilibrates with the presence of exchangeable inorganic metal cations such as Ca^{+}, Na^{+}, and Mg^{2+} located in the interlamellar space (Parolo, Pettinari, Musso, Sánchez-Izquierdo, & Fernández, 2014).

Today, many methods have been studied to increase the adsorption capacity of natural bentonite for contaminant removal from wastewater. Commonly, the clay materials can be modified by both physical and chemical treatment. Bentonite modification by thermal activation has increased the nature of bentonite as an adsorbent for dyes and heavy metals removal from aqueous solution. Thermally activated bentonite has been proved to be a highly efficient adsorbent for Congo red removal from wastewater (Toor, Jin, Dai, & Vimonses, 2015). Bentonite modification by chemical treatment has been widely developed, as reported in many publications (D'Amico, Ollier, Alvarez, Schroeder, & Cyras, 2014; Jing, Hou, Zhao, Tang, & Wan, 2013; Marsal, Bautista, Ribosa, Pons, & García, 2009; Mishra & Mahato, 2016).

The term "acid activation" represents one of the chemical treatments used on bentonite to produce the partially dissolved bentonite. By treating the bentonite with inorganic acids, the inorganic cation lying in the interlayer structure of bentonite will be replaced with the monovalent hydrogen ion. This replacement also leaches out the ferric, ferrous, aluminium, and other trace cations, so the smectite layer of the bentonite will be altered, and the specific surface area and the porosity will be increased (Komadel, 2016). This method is the most common preliminary chemical modification of clay and clay minerals especially bentonite for use in both scientific and industrial purposes.

In this work, the abundant natural bentonite from Sarolangun district, Jambi Province, Indonesia was prepared and activated by the acid-activation method using H_2SO_4 as an acid agent in order to elevate its natural properties such as the surface area and adsorption capability. The objective of this work was to investigate the feasibility of the local bentonite from Sarolangun to be treated by the acid-activation method and used as an adsorbent material for Congo red removal.. The adsorption behavior and effect of the experimental parameter including the adsorbent amount, contact time, dye concentration, and adsorption temperature were also investigated.

2. Materials and methods

2.1. Chemicals and instrumentation

Bentonite used in this work was natural bentonite from the Sarolangun deposit in Jambi Province, Indonesia. Sulfuric acid (H_2SO_4) as an acid activator agent for bentonite was purchased from Sigma Aldrich. It is analytical reagent grade and used as received without further treatment or purification. Congo red as artificial dye adsorbate was purchased from Merck and used without further treatment. The adsorbent characterization using XRD was conducted using X-Ray diffraction on a Rigaku Miniflex 600 instrument equipped with Ni-filtered CuKα radiation with scanning speed 5° min^{-1}. FTIR analysis was carried out by FT-IR, a Shimadzu Prestige-21 instrument using KBr disc with a wavenumber 400–4000 cm^{-1}. Nitrogen adsorption-desorption isotherm analysis was conducted with an ASAP Micromeritics 2020 surface area analyzer. X-ray fluorescence analysis was carried out with a PANanytical type Minipal 4. Congo red concentration after the adsorption process was measured using a double beam UV-Vis spectrophotometer instrument from EMCLab type EMC-61PC-UV.

2.2. Natural bentonite activation and characterization

The natural reddish bentonite obtained from Sarolangun deposit, Indonesia, was used as the source material in order to form adsorbent to remove the Congo red dye. Before acid activation, the natural bentonite first was washed using distilled water three times in order to remove the impurities. The wet cleaned bentonite was dried at 378 K for eight hours and mashed in a porcelain mortar to enable passage through a 100-mesh standard ASTM sieve. The resulting material was then labelled as natural Sarolangun bentonite (NSbent).

The acid-activated bentonite was prepared based on the work carried out by Önal and Sarikaya (2007), using the wet chemical method. Prior to the

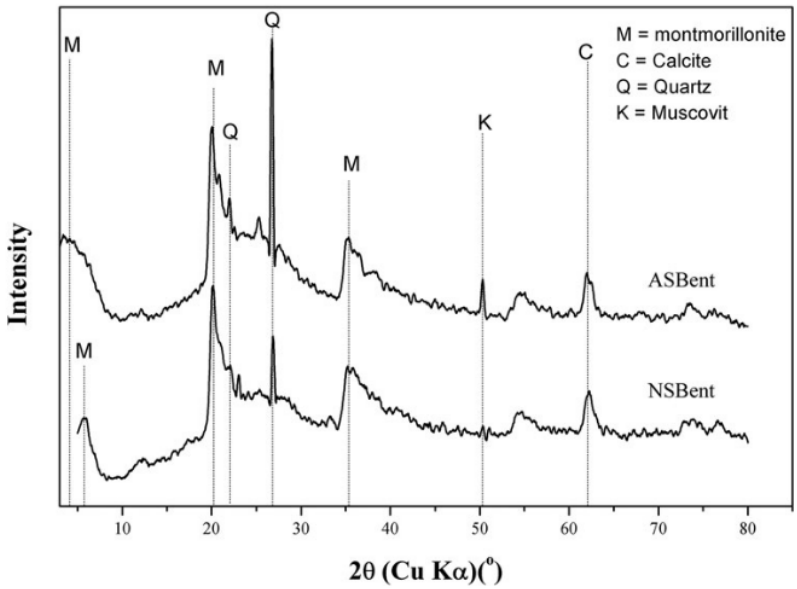

Figure 1. XRD patterns of natural Sarolangun bentonite (NSbent) and acid activated Sarolangun bentonite (ASbent) by various acid concentrations.

activation process, the NSbent samples were dried at 378 K for four hours, then 20 g of samples were mixed with 400 mL of H_2SO_4 solution (10% by mass) for six hours at 363 K by stirring in a 1000 mL flask. After the acid treatment, the suspension was filtered and the precipitate washed using distilled water to remove the excess of SO_4^{2-} ions. The acid treated NSbent was then dried at 378 K for eight hours and stored in a closed glass bottle. The acid-activated bentonite product was labelled as acid-activated "Sarolangun bentonite (ASbent)". Changes of bentonite properties before and after activation by H_2SO_4 were investigated using X-ray diffraction (XRD), FT-IR, N_2 adsorption-desorption, and X-ray fluorescence.

2.3. Adsorption experiment

The adsorption of Congo red onto the ASbent was thoroughly examined using the batch adsorption system. Congo red stock solutions (1000 mg L^{-1}) were prepared by dissolving 1 g Congo red powder in 1000 mL of distilled water. The working solution of Congo red was made by diluting the stock solution into the desired concentration with distilled water. Typically, 0.05 g of ASbent was added into a 100-mL conical flask containing 50 mL of Congo red solution of the predetermined concentration. The mixture was then stirred at 400 rpm at room temperature for a predetermined contact time. After this process, the mixture was separated using a centrifuge at 4000 rpm for five minutes. The remaining Congo red concentration was then determined using a spectrophotometer. The percent removal and the adsorption capacity of the adsorption process were calculated by equation (1) and (2), respectively.

$$\%removal = \frac{C_0 - C_t}{C_0} x100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)}{m} V \quad (2)$$

where C_o, C_t, q_t, V, and m are the initial Congo red concentration (mg L^{-1}), Congo red concentration after desired contact time t (mg L^{-1}), adsorption capacity (mg g^{-1}), volume of the Congo red solution (L), and the amount of adsorbent used (g), respectively.

3. Results and discussion

3.1. Adsorbent characterization

The natural bentonite from Sarolangun (NSbent) was activated by sulfuric acid as a facile activation method. The NSbent and acid-activated bentonite from the Sarolangun (ASbent) samples had been subjected to powder X-ray diffraction analysis in order to study the change of the bentonite structure resulting from the activation process. The X-ray diffraction pattern for both NSbent and ASbent are presented in Figure 1. The result of the XRD analysis for NSbent showed that the used natural bentonite consists of montmorillonite, calcite, quartz, and muscovite minerals. The XRD pattern of the NSbent sample revealed the presence of the d_{001} reflection of the

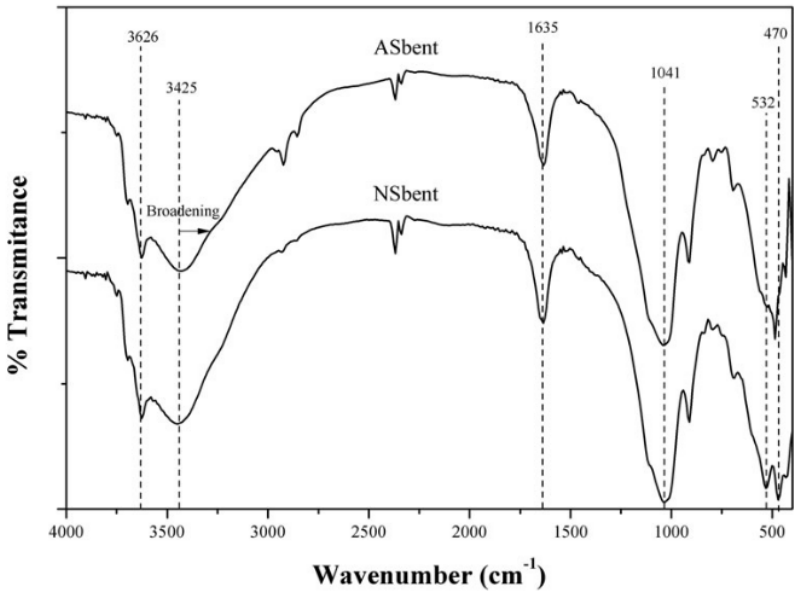

Figure 2. FTIR spectra of natural Sarolangun bentonite (NSbent), and activated Sarolangun bentonite (ASbent).

bentonite interlayer, which is present in 2θ about 5.72° with the basal spacing value of 1.51 nm. The presence of d_{100} reflection of the montmorillonite interlayer appeared at 2θ around 20°. The sharp reflection pattern emerged in the 2θ about 27° revealed the presence of quartz as impurities (Faghihian & Mohammadi, 2013).

After the acid activation, the XRD pattern of ASbent showed the broadening of the d_{001} reflection indicating that the layered structure of NSbent was partially destroyed due to acid activation, and also the crystallinity of the ASbent was affected (Pawar, Bajaj, & Lee, 2016). Moreover, the XRD pattern showed that after the acid activation, the 2θ reflection at 5.72° was shifted left to 4.16° (basal spacing increased from 1.51 to 1.99 nm). This phenomenon revealed a significant collapse of the crystalline structure. The increase of the quartz (Q) reflected at 2θ around 27° after the acid activation process showed that quartz as impurities was not destroyed in the process and the intensity was increased due to the smectite structure of the bentonite being partially destroyed.

In order to investigate the change in bentonite structure after the acid activation, FTIR spectroscopy was conducted due to its high sensitivity to the modification of the clay structure. During the acid activation, the proton from the acid penetrated into the bentonite layers and attached the OH group. As the dihydroxylation and partial dissolution of the smectite structure occurred, the changes in the characteristics of the absorption bands of the OH vibration will be recorded in IR spectra. The FTIR spectra NSbent and ASbent are shown in Figure 2. The characteristic vibration peaks of the NSbent were recorded at wavenumber 470, 532, 910, 1041, 1635, 3425, and 3626 cm^{-1} (Pawar et al., 2016). The two adjacent vibration peaks observed at 3425 and 3626 cm^{-1} were attributed to the stretching vibration band of the OH section of the hydroxyl group on the bentonite structure and the water molecules present in the interlayer space (Tomul, 2011), The band observed at the wavenumber 1635 cm^{-1} was also attributed as the OH deformation vibration from the water molecule (Kumararaja, Manjaiah, Datta, & Sarkar, 2017). After the acid activation, as can be seen in Figure 2, the band at 3425 cm^{-1} which was broadened as the effect of the introduction of the –OH group due to the partial dissolution of the main bentonite structure.

The sharp vibration band at wavenumber 1041 cm^{-1} is reported as the stretching vibration of Si-O group (He et al., 2012). Due to the dissolution during the acid activation, the band of the Si-O group decreased. The NSbent spectra showed the specific vibration band of the Al-O-Si group recorded at wavenumber 532 and 470 cm^{-1} as the stretching and bending vibration band (Kumararaja et al., 2017), while for the ASbent spectra, the vibration band at 530 cm^{-1} was not observed and the band at 470 cm^{-1} was shifted to 486 cm^{-1}. As reported by Özcan and Özcan (2004), this phenomenon is an indication that the layers structure remains after the activation process.

The N_2 adsorption-desorption analysis has been subjected to the NSbent and ASbent samples to

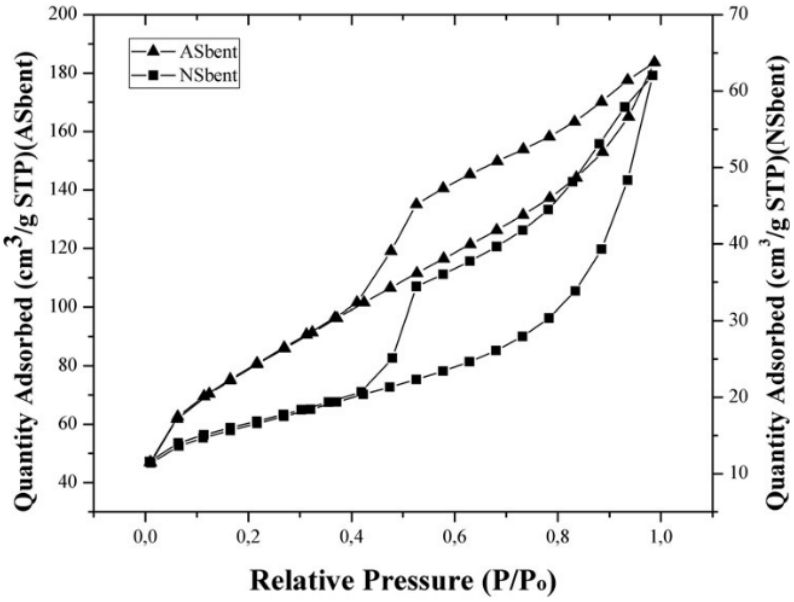

Figure 3. N_2 Adsorption desorption isotherm of NSbent and ASbent.

investigate the change of the textural properties during the acid activation process. The N2 adsorption-desorption isotherm for the NSbent and ASbent samples is presented in Figure 3. The results clearly illustrate that the isotherm pattern of these samples follows the type IV based on IUPAC adsorption isotherm classification. The further data of the NSbent and ASbent textural properties areshown in Table 1. The obtained data showed that the acid activation process has significantly elevated the surface properties of the natural bentonite. The ASbent has five-fold higher surface area than the NSbent. The pore volume of ASbent was also increased three-fold compared with the NSbent. The increasing quality of the textural properties after acid activation occurs because particles inside the dissolved octahedral sheets were split (Pawar et al., 2016).

The result of the XRF analysis of NSbent and ASbent samples are depicted in Figure 4. Both NSbent and ASbent are mainly constructed by Al_2O_3 and SiO_2, with the presence of trace elements of various metal oxides. The results clearly show that the acid activation process successfully changed the chemistry of the natural bentonite. After acid activation, the abundance of some metallic oxides particularly Fe_2O_3, TiO_2, MnO, V_2O_5, NiO, CuO, and ZnO was reduced. This phenomenon indicates that these metal oxides, which correspond to the inorganic interlayer cation, were dissolved readily during the acid activation process, while the abundance of Al_2O_3 was not changed and SiO_2 was significantly increased. This finding shows that the layered structure of the bentonite constructed by Al_2O_3 and SiO_2 provides much resistance to the acidic condition. The increase of the SiO_2 content was caused by the reduction of other cations that lie in the interlayer and octahedral sheets (Elfadly, Zeid, Yehia, Abouelela, & Rabie, 2017).

Table 1. The textural properties of bentonite samples based on N_2 adsorption-desorption isotherm.

Properties	Samples	
	NSbent	ASbent
BET Surface Area ($m^2\ g^{-1}$)	55.8719	278.7961
Langmuir surface area ($m^2\ g^{-1}$)	231.9062	820.6051
BJH surface area ($m^2\ g^{-1}$)	39.546	209.795
Total Pore volume ($cm^3\ g^{-1}$)	0.0959	0.2841
Micropore volume ($cm^3\ g^{-1}$)	0.0069	0.0118
Average pore width (nm)	6.8710	4.0770
BJH pore diameter (nm)	8.7765	4.7021

3.2. Effect of initial pH

As one of the diazo class dyes, the form of the Congo red molecule in the aqueous solution will be affected by the pH value. As mentioned by Lian, Guo, & Guo (2009), the color of Congo red changed significantly from red to dark blue when the pH of the solution was reduced to 2. On the other hand, when the pH of Congo red solution was adjusted to be more than 10, its color was different from the original. Hence, in this work, the effect of initial pH solution on the adsorption of Congo red on ASbent was studied at a pH ranging from 5 to 9 for an initial concentration of Congo red of 100 mg/L. Figure 5 shows the effect of initial pH of Congo red solution toward the adsorption capacity of ASbent. The results indicate that the adsorption of Congo red on

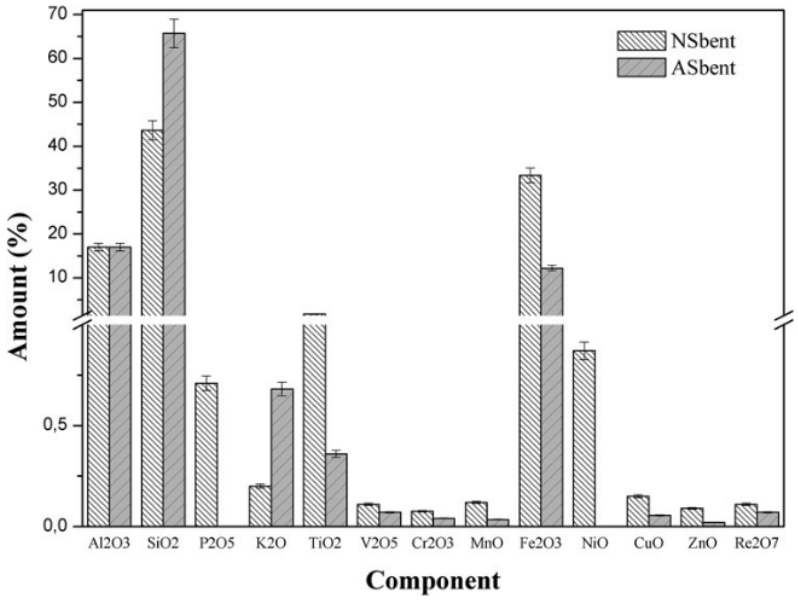

Figure 4. XRF analysis result for NSbent and ASbent samples.

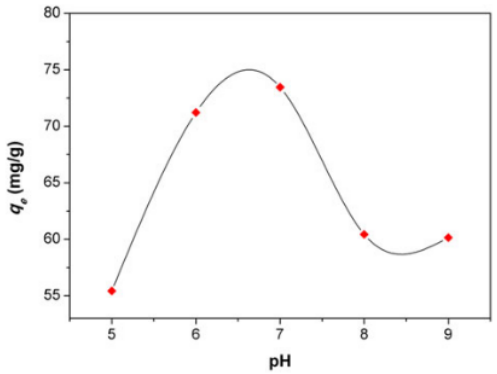

Figure 5. Effect of initial pH on the adsorption capacity (q_e).

ASbent was profoundly affected by the pH of the solution. The most favored adsorption process occurred at a neutral pH (pH 6 to 7). By increasing the pH to be more than 7, the adsorption capacity decreased then remained relatively constant after pH 8. Moreover, below pH 6 (acidic condition), the adsorption capacity also decreased by decreasing the solution pH.

3.3. Effect of adsorbent dosage

The effect of the adsorbent amount on Congo red adsorption was tested by contacting various amounts of the adsorbent with 50 mL of 50 mg L^{-1} Congo red solution at room temperature for 30 min. The result of the experiment in the form of a graph of the amount of adsorbent dosage against percent removal and adsorption capacity (q_e) is presented in Figure 6. The graph describes that by increasing the amount of adsorbent, the percent removal of Congo red on ASbent was also gradually increased, while for the adsorption capacity, the result showed that the maximum adsorption capacity was reached when the adsorbent dosage was in the range of 0.05 to 0.1 g. As the adsorbent amount increased, the number of active sites available during the adsorption increased as well, and thus the percentage of the removal also increased since all active sites may not be available during the adsorption due to the overlapping between the active sites themselves, and so the adsorbed amount of the adsorbent decreases.

3.4. Adsorption kinetic study

In this work, the adsorption kinetic study was conducted by several batch adsorption experiments at various contact times. 0.05 g of ASbent had contact with 50 mL of 50 mg L^{-1} Congo red solution, which was then agitated using a magnetic stirrer for different contact time in the range of 0 to 60 min at room temperature. Figure 7 shows the effect of contact time on the adsorption capacity of the activated bentonite adsorbent. The graph indicates that the adsorption of the Congo red on activated bentonite rapidly occurred in the first 5 min' contact time and gradually slowed down after 10 min' contact time until the adsorption process attaining equilibrium state within 30 min.

Similar outcomes to these results were also reported in our previous work (Taher, Mohadi,

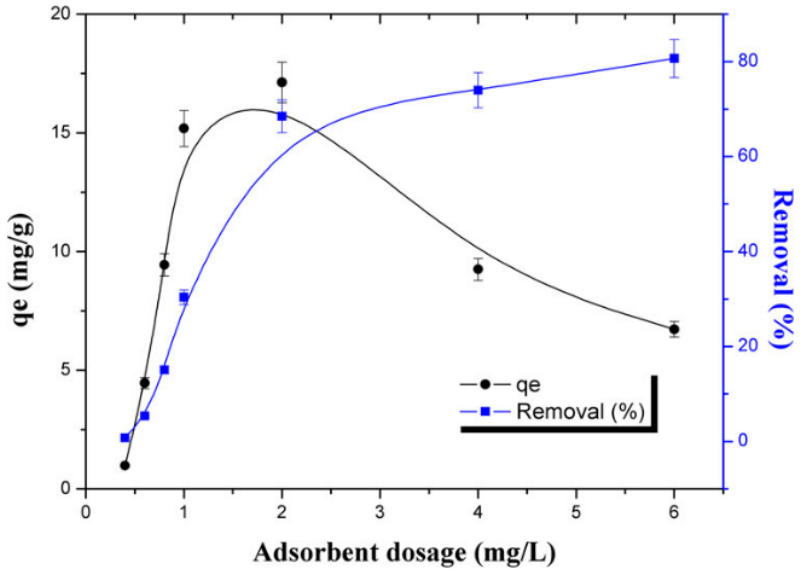

Figure 6. Effect of adsorbent dosage on the percent removal and adsorption capacity of Congo red onto ASbent adsorbent.

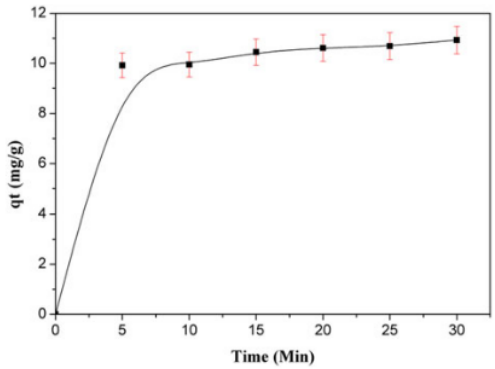

Figure 7. Effect of contact time on the adsorption capacity of Congo red onto activated bentonite.

Rohendi, & Lesbani, 2017) and many articles before that (Du et al., 2017; Goswami and Phukan, 2017; Rostami, Kaya, Gür, Onganer, & Meral, 2015). These indicated that, in the beginning, the Congo red molecules were adsorbed on the exterior surface of the activated bentonite adsorbent. The rapid adsorption during the first stage of adsorption was due to the most active site of the bentonite being unoccupied. After most of the adsorbent active sites had been occupied, the force between the Congo red as adsorbate with the adsorbent was gradually decreased and caused a reduction in the speed of adsorption. After the active exterior sites of the adsorbent had been entirely fulfilled, the adsorption process continues into the interior active sites of the adsorbent particles or into the interlayers of the bentonite; this process takes a relatively long time (Wang, Zheng, Deng, Feng, & Fu, 2013).

The adsorption rate constant and the adsorption mechanism of Congo red on ASbent was investigated based on the pseudo-first-order and pseudo-second-order kinetic model. The pseudo-first-order kinetic model was developed for the adsorption of solid/liquid system that suggested by Lagergren (Source). The equation for the pseudo-first-order kinetic model is described as follows:

$$dq/dt = k_1(q_e - q_t) \tag{3}$$

By integrating the equation with initial condition $q_t = 0$ at $t = 0$, the equation can be transformed into a linear equation under boundaries conditions as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 \tag{4}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where q_e and q_t are the amount of Congo red adsorbed at equilibrium and at any time t (mg g^{-1}), respectively. The pseudo-first-order kinetic rate constant is represented as k_1. The pseudo-first-order constant was measured by plotting the $\log(q_e - q_t)$ against t.

The pseudo-second-order kinetic model was investigated based on the assumption that the adsorption experiments have been carried out in the equilibrium condition. The mathematical equation for the pseudo-second-order kinetic model is presented as follows:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \tag{6}$$

The linear form of the equation can be presented by integrating the equation with the initial condition of $q_t = 0$ at $t = 0$ as follows:

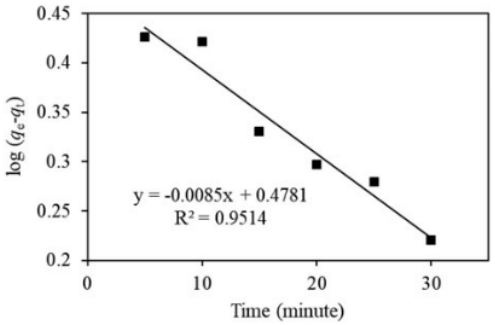

Figure 8. Plot Time versus log (q_e-q_t).

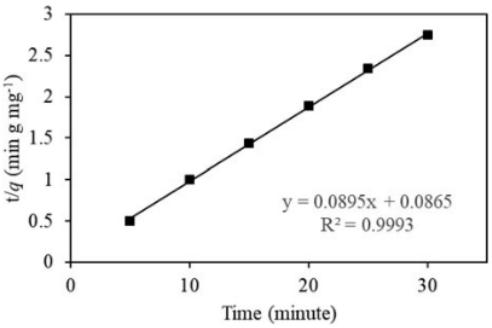

Figure 9. The plot times against t/q.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_2 is the pseudo-second-order rate constant, q_e and q_t are the amounts of Congo red adsorbed at equilibrium and at any time t (mg g^{-1}), respectively.

The result for the pseudo-first-order and pseudo-second-order kinetic model of Congo red on ASbent is presented in Figures 8 and 9, respectively. The comparison of both figures describes that the coefficient correlation for the plot of the pseudo-second-order equation is higher than the pseudo-first-order kinetic model. The coefficient correlation (R^2) value is 0.9514 for the pseudo-first-order kinetic model, and 0.9993 for the pseudo-second-order kinetic model. This finding reveals that the adsorption of Congo red on ASbent was better described based on the pseudo-second-order kinetic than the pseudo-first-order kinetic model. Since the pseudo-second-order kinetic model was based on the equilibrium capacity, this result also revealed that the adsorption rate of the Congo red on ASbent depends on the dye concentration at the ASbent surface at equilibrium (Wang & Wang, 2008). This finding also described that the rate determining step of Congo red adsorption on ASbent was a chemisorption (El Haddad et al., 2014b). The overall value of the kinetic study of Congo red on ASbent is presented in Table 2.

Table 2. Constant of kinetic models of Congo red removal by ASbent.

Kinetic Model	Parameters	Congo red
Pseudo-first-order	q_e experimental (mg g^{-1})	12.5
	q_e calculated (mg g^{-1})	3.0
	k_1 (min^{-1})	0.0195
	R^2	0.9513
Pseudo-second-order	q_e experimental (mg g^{-1})	12.5
	q_e calculated (mg g^{-1})	11.1787
	K_2 (g/mg min)	0.0925
	R^2	0.9992

3.5. Adsorption equilibrium study

The design of the adsorbate adsorption can be optimized by looking up the most appropriate correlation of the equilibrium curve. The adsorption isotherm described the equilibrium between the adsorbate that was adsorbed onto the active site of the adsorbent and the adsorbate retained in the solution. Previously, many adsorption isotherm models have been developed such as Langmuir (1918), Freundlich (1907), Redlich and Peterson (1959), Temkin, Dubinin-Radushkevich. However, the most frequently used models were Langmuir and Freundlich models (Božić et al., 2013). Here, in this experimental work, the adsorption isotherm was studied based on these Langmuir and Freundlich models to explain the relation between dye adsorbed on the adsorbent and the concentration of the dye in the liquid phase (Wang, Pan, Cai, Guo, & Xiao, 2017).

The Langmuir isotherm model is the most widely used adsorption isotherm model applied for adsorption of any substance, in particular for pollutants removal from aqueous solutions. (Bulut, Özacar, & Şengil, 2008). The general Langmuir isotherm equation is presented in equation (8) as follows:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (8)$$

The linear form of the equation (8) is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (9)$$

where K_L and q_m are the Langmuir constant based on the adsorption energy (L mg^{-1}) and the maximum amount of adsorption related to complete monolayer coverage on the surface of the adsorbent (mg g^{-1}).

The prediction about the affinity between the adsorbate and the adsorbent (adsorption favorability) also can be predicted from the Langmuir parameter based on the dimensionless separation factor (R_L) that is defined by equation 10 as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

where K_L and C_0 are the Langmuir constant (L g^{-1}) and initial concentration of Congo red as adsorbate

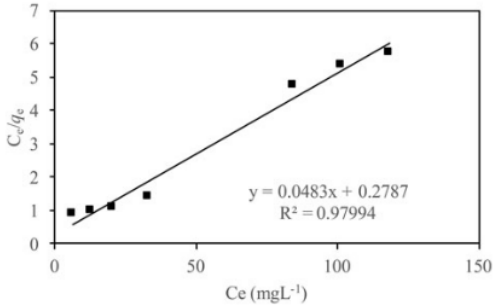

Figure 10. Plot C_e versus C_e/q_e.

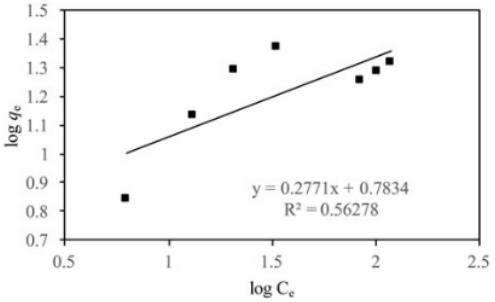

Figure 11. Plot log C_e versus log q_e.

(mg L^{-1}), respectively. The value of R_L was used to predict the isotherm type of the adsorption which occurred. If the RL value is higher than 1 ($R_L > 1$), it means that the adsorption is unfavorable. If the R_L value is less than 1 ($R_L < 1$), it means that the adsorption process is linear. The adsorption is favorable if the R_L value is higher than zero and less than 1 ($0 < R_L < 1$), and the adsorption is irreversible if the RL value is equal to 0 ($R_L = 0$) (El Haddad, Slimani, Mamouni, ElAntri, & Lazar, 2013; Xiyili, Çetintaş, & Bingöl, 2017).

The Freundlich isotherm model is one of the adsorption isotherm models that can be used to predict the adsorption capacity of the adsorbent. The mathematical equation for the Freundlich isotherm model is presented as follows:

$$q_e = k_f C_e^{\frac{1}{n}} \tag{11}$$

The equation can be transformed into the linear form as follows:

$$\log q_e = \frac{1}{n}\log C_e + \log k_f \tag{12}$$

where k_f is the constant of the Freundlich model which corresponds to the adsorption capacity, and n is defined as the heterogeneity factor. Further, the n value can be used to predict the probability of the adsorption process, where with $n > 1$ it means that the adsorption process was favorable. The useful value of k_f and n can be determined based on the intercept and slope of the linear plot of log q_e against log C_e.

The plot of the linear form for the Langmuir and Freundlich isotherm model is presented in Figures 10 and 11, respectively. Both figures show the coefficient correlation (R^2) of the data conformi to the Langmuir and Freundlich isotherm model. The result showed that the Langmuir isotherm model was better described by Langmuir isotherm, which has higher R^2 value (further confirmed in Figure 12). The R^2 value for the Langmuir isotherm model is calculated as 0.9799, while the Freundlich model is 0.652. The whole adsorption kinetic parameter based on the Freundlich and Langmuir model is illustrated in Table 3.

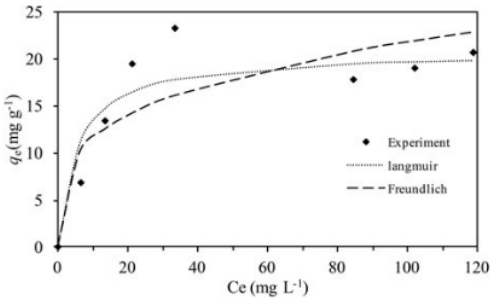

Figure 12. Adsorption isotherm of Congo red onto ASbent fitted by Langmuir and Freundlich model.

Table 3. The adsorption isotherm parameters for Congo red adsorption onto ASbent.

Langmuir Isotherm				Freundlich Isotherm		
q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F	n	R^2
20.7039	0.1794	0.0336–0.2179	0.9799	6.0729	3.6088	0.5627

3.6. Thermodynamic properties

Temperature is an important parameter of the thermodynamic adsorption properties. The effect of adsorption temperature toward the Congo red adsorption onto ASbent was investigated at various temperatures (303, 313, 323, and 333 K). The adsorption data were then used to determine the thermodynamic parameters of the adsorption process including the change of Gibb's free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0). The value of these three basic thermodynamic parameters was measured by the following equation:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{13}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{14}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

The value of the change of enthalpy (ΔH^0) and entropy (ΔS^0) was calculated as the slope and intercept of the linear plot ln(q_e/C_e) versus 1/T,

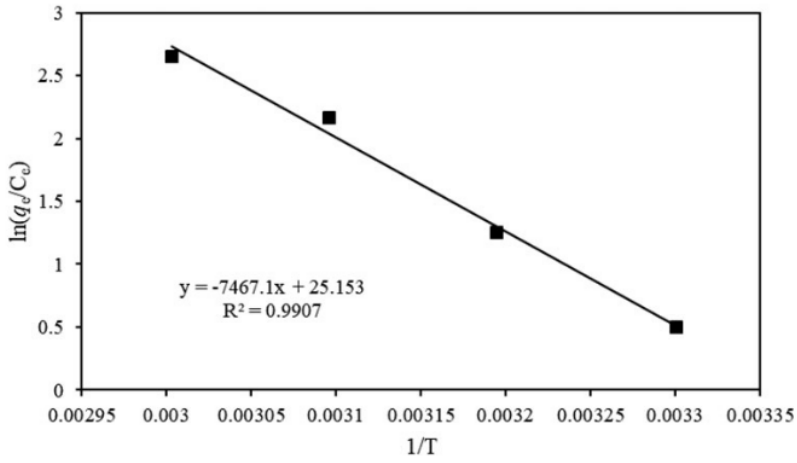

Figure 13. Plot of $\ln(q_e/C_e)$ against 1/T for Congo red adsorption onto ASbent.

Table 4. Thermodynamic parameters of Congo red adsorption onto ASbent.

ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔG^0 (kJ/mol)			
		303 K	313 K	323 K	333 K
62.081	209.122	−1.246	−3.336	−5.426	−7.516

respectively. As depicted in Figure 13, the coefficient correlation for the linear plot of ln(q_e/C_e) against 1/T was more than 0.98. It indicates that the linear equation obtained has good regression value. The values of the basic thermodynamic parameters are presented in Table 4. ΔH^0 and ΔS^0 values for Congo red adsorption onto activated bentonite were 62.081 kJ mol^{-1} and 209.122 J mol^{-1} K^{-1}, respectively. The positive value for the change of the enthalpy (ΔH^0) indicates that the adsorption is undergoing the endothermic process. Also, the positive value of the change of entropy (ΔS^0) revealed that the during the adsorption process, the randomness of the solid-solution interface was increased (El Haddad et al., 2014a; Xiyili et al., 2017).

As shown in Table 4, the negative value of the ΔG^0 indicates that the Congo red adsorption onto ASbent is a spontaneous process (Slimani et al., 2014). Moreover, the result showed that by increasing the adsorption temperature, the ΔG^0 values gradually decreased. This phenomenon indicates that the adsorption process is more favorable at high temperatures. (Maleki, Hayati, Najafi, Gharibi, & Joo, 2016). Generally, the ΔG^0 value for physical adsorption is in the range of 0 to −20 kJ mol^{-1}, while the ΔG^0 value for the chemical adsorption is in the range of −80 to −400 kJ mol^{-1} (Liu, Zheng, Wang, Jiang., & Li, 2010). The result of ΔG^0 value for the adsorption as described in Table 4 is in the range −1 to −7 kJ mol^{-1}. This result indicates that the Congo red adsorption onto activated bentonite follows the physical adsorption mechanism.

4. Conclusion

Acid-activated bentonite prepared from natural bentonite Grounded from the Sarolangun deposit, Jambi Province, Indonesia was investigated in terms of its adsorption capability to remove Congo red from aqueous solution. The characterization of the natural bentonite sample before and after acid treatment showed that the structure of the natural bentonite was successfully modified. The maximum adsorption capacity of the ASbent based on the adsorption isotherm study was noted as 20.7 mg g^{-1}. The result of the adsorption kinetic study revealed that the pseudo-second-order kinetic model is more appropriate than the pseudo-first-order kinetic model. For the adsorption isotherm model, based on the experiment data, the Langmuir isotherm model is fit well to illustrate the adsorption isotherm of the Congo red onto ASbent.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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