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Synthesis and Characterization of Activated Sludge/Zeolite Adsorbent for Lampung Textile Industry Wastewater Treatment

Synthesis and Characterization of Activated Sludge/Zeolite Adsorbent for Lampung Textile Industry Wastewater Treatment

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Abstract. The present study reports a green synthesis method for ordered adsorbent material for Lampung Ethnic Textile Industry (LETI) wastewater treatment from activated sludge rubber industry and clipnotilolite (natural zeolite). LETI wastewater is containing about 70 mg/L of Chromium; 63,600 mg/L of COD and 36,500 mg/L of BOD. It has also high colour intensity and complex pollutants. Adsorbent can reduce Chromium heavy metal significantly. Activated sludge/zeolite adsorbent was calcined by furnace at 600°C for 15 min. It was activated by 10% wt/wt of NaOH and 1 molar of HCl. The material properties of calcined activated sludge/zeolite adsorbent was characterized by FT-IR, BET and SEM. Results showed that structure interaction processes occured between activated sludge and zeolite clipnotilolite. The BET analysis results showed that surface area, pore volume and average pore size respectively are 932 m^2/gram; 0.6 cc/gram; and 258.87 Å.

1. Introduction

Wastewater from industrial process especially textile industries contain many inorganic and organic contaminants such as acidic, caustic dissolve solids, toxic compounds, dyes, and heavy metals [1]. Wastewater can cause serious environmental problems if it is not treated well by industries[2]. One of effective methods for minimizing the hazardous effect of wastewater effectively is adsorption method. This method is more lucrative than other conventional methods because of lower initial cost, simplicity in design, ease to operation, and no toxic [3]. The material that used for adsorption is activated carbon.Activated carbon is very useful for removing various pollutants because it has large specific surface area and pores. However, activated carbon is expensive because it must be added by other components to increase adsorptive capacity[4].

The alternative material that can be used as resources for adsorbent is sludge from rubber industry. A large volume of sludge is generated by rubber industries every year. Sludge is a carbon-rich, renewable, low cost and vast resources [5]. Activated sludge has been proven to reduce BOD [6], heavy metal [7] and polyacrylate[8] in wastewater. The macromolecules (protein, polysaccharides, nucleic acids, humic-like substance, uronic acids and lipids) in activated sludge play important role for adsorption of heavy metal [9]. However, activated sludge has a small adsorptive capacity when it is not modified with additives because of its of low surface area. One of the solution to increase surface area of activated sludge is to mix activated sludge with zeolites. Zeolites are porous aluminosilicate minerals made from interlinked tetrahedral of alumina (AlO_4) and silica (SiO_4). Framework structure of zeolite is negatively charged consequently zeolites can adsorb cations such as Pb^{2+}, Cd^{2+} and Cu^{2+}[10].The aims of this work are to investigate the characteristic of activated sludge-zeolite adsorbent and to evaluate its adsorptive capacity for removing waste parameters of dye solution from ethnic textile industry in Bandar Lampung. The characteristics of activated sludge-zeolite adsorbent will be analyzed using with Branuar Emeet and Teller (BET), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectrometer (FT-IR). The experimental result will then be analyzed using several kinetic and isotherm models.

2. Materials and Methods

2.1. Materials

Sludge used in this study was collected from PT. Perkebunan Nusantara VII (South Lampung, Lampung). Zeolite was purchased from CV. Minatama (Bandar Lampung, Lampung) and batik dye wastewater was obtained from Lampung ethnic textile industry.

2.2. Methods

2.2.1. Preparation of Activated Solid Waste

The sludge obtained was dried at 110^{o}C for 24 h in oven. The dried sludge then sieved to particle size range 100 mesh. Activated sludge was prepared via two steps: calcination and soaking step. The calcination step did by drying dried sludge at 600^{o}C for 15 minutes in the absence of air using a Thermolyne muffle furnace 6000. The soaking step did by soaking the calcined sample with certain volume of NaOH (100 g of calcined sample with 500 ml of NaOH (10%)) for 24 h at room temperature. After soaking step, sample was separated using Whatman filter paper. Prepared sludge was washed with distilled water till neutral filtrate and then dried at 100^{o}C then for 6 h and finally stored in desiccator.

2.2.2. Preparation of Lampung Natural Zeolite

Initially, natural zeolite was grinded and separated in particle size ±100 mesh. The separated zeolite was washed and soaked with distilled water for 24 h in order to remove residue, and then dried in an oven at 100^{o}C for 24 h. One hundred grams of natural zeolites soaked in 500 ml HCl 1 M under magnetic stirring for 3 h. The solution of activated zeolite was filtered with Whatman filter paper. The activated zeolite was then washed with distilled water in order to remove activating agent, and then placed in oven at 105^{o}C for 3 h and kept in desiccator.

2.2.3. Preparation of Adsorbent Molding

The adsorbent was shaped in the cylindrical mold with a size 0.5 x 0.7 cm by mixing activated sludge and activated zeolite with a mass ratio (gram) 3:2, 4:1 and 5:0. Tapioca flour, clay, and sodium silica were used as a binder, each ratio used 5 gr of binder. After molding step, the adsorbent was dried in oven at 150^{o}C for 1 h.

2.2.4. Characterization of Adsorbent

The characterization of adsorbent was performed using different technique. The surface morphology and area of materials were performed using SEM and BET. Functional group of the materials were investigated by FT-IR.

2.2.5. Adsorption Experiment

Based SEM characteristic the ratio which has the largest surface area will be considered as the best adsorbent. Later, this adsorbent was placed in a glass container with dye solution from Lampung ethnic textile industry to estimate the reduction of Cr concentration and the other indicators such as chemical oxygen demand (COD), biological oxygen demand (BOD), turbidity, color, pH and total suspended solid (TSS). Batch experiments were run by mixing 10%, 15% and 20% (w/v) of adsorbent sample in 100 mL of dye solution. The samples were then agitated using magnetic stirred at 180 rpm. For determining the time required to reach equilibrium, each batch was prepared and analyzed after time interval (30, 60, 90, 120, 150) min. The solutions were filtered to separate the remaining solution and adsorbent. The remaining concentrations of each solution were measured by visible spectrophotometer to estimate reduction of Cr concentration. The amount adsorbed of Cr concentration onto adsorbent (q_e) can be estimated by the following equation:

$$qe = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

Where q_e is the amount of Cr adsorbed per unit mass of adsorbent (mg/g), Co and Ce (mg/l) are initial and equilibrium Cr concentration, V(L) is the volume of dye solution, and m(g) is the adsorbent mass.

3. Results and Discussion

3.1. BET Surface Area

The BET surface area, pore volume and pore size of adsorbent with different ratio between activated sludge and activated zeolite summarized in Table 1. The BET surface area and average pore size of activated sludge for ration of (5:0) was 768.454 m^2/g, 18.825 Å respectively. After modification with activated zeolite (4:1), the BET surface area and average pore size was increased from 768.454 to 832.2 m^2/g and 18.825 to 128.32 Å. Adding more zeolite (3:2) increased more surface area and average pore size from 832.2 to 923 m^2/g and 128.32 to 258.872 Å. From this result shows that adding activated zeolite increased specific pore size of the adsorbent [11]. According to the average size of pores, the activated sludge-zeolite adsorbent consists of many mesoporous sites. These type of pores are very important to adsorb ions and macromolecules [12].

Table 1. Textural Properties of Activated Sludge-Zeolite Adsorbent

Ratio	BET specific surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)
3:2	923	258.872	0.6
4:1	832.2	128.32	0.534
5:0	768.454	18.825	0.723

3.2. Chemical Surface Characterization

The FT-IR spectra (4000-600 cm^{-1}) of activated sludge-zeolite adsorbents with varied ratio were shown in Figure 1. According to the result, activated sludge-zeolite adsorbent at ratio 5:0 has lower peak compared to adsorbent at ratio 4:1 and 3:2 for the peak around 3360-3370 cm^{-1}. The band at 3000 to 3500 cm^{-1} indicates the presence O-H group [4]. Ratio 4:1 showed the small peak at absorption band between 2900 and 2800 cm^{-1} however at ratio 3:2 and 5:0, it did not show the peak. The band at 2922 and 2850 cm^{-1} are stretch of alkyl C-H [13], which indicates waxes [14]. Additionally, another peaks appeared at ratio 3:2 and 5:0 at the band between 1670 to 1740 cm^{-1} but it did not appear at ratio 4:1.

The peak's band at 1680 to 1740 cm^{-1} is assigned to C=O carbonyl groups and band at 1670 cm^{-1} indicates carboxylic groups. All the ratio of the adsorbents have a small peaks at the broadband at around 1500 to 1600 cm^{-1} which is indicated the absence of carboxylic group and NH. The presence of carboxyl group indicated that adsorbents have the highest capacity to adsorb heavy metal [3]. C-O-C group stretches from 1070 to 1010 cm^{-1} and it indicates polysaccharide [15] while C-O stretches at

1029 cm^{-1}[14]. These bands appeared at all the ratio of adsorbent. The band from 700 – 800 cm^{-1} can be assigned as Si-C group [10]. Adsorbent at ratio 3:2 has more Si-C group than the other ratio, which can be shown from the band at 786.47 cm^{-1}. For ratio 4:1 and 5:0 the bands are at 783.74 and 783.92 cm^{-1}. The height of the peak at ratio 3:2 is linear with adding more zeolite in the mixture of adsorbent.

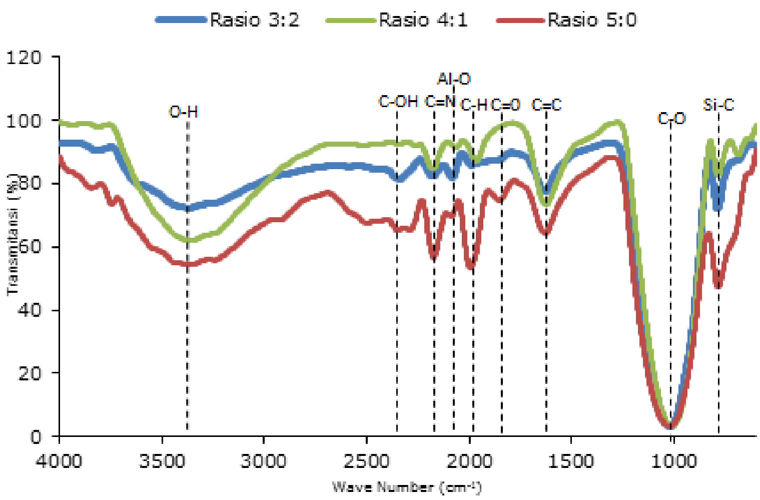
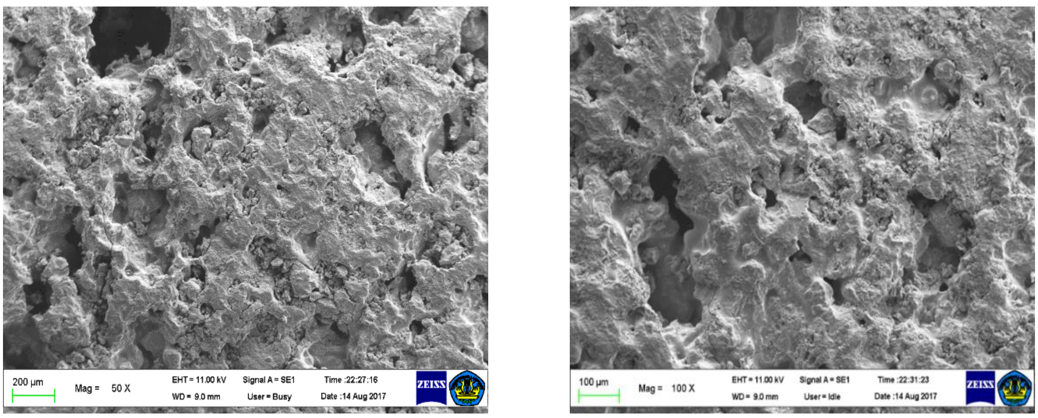


Figure 1. FT-IR Spectra of Activated Sludge-Zeolite Adsorbent

3.3. Morphology

The surface morphology of the best adsorbent with ratio 3:2 was investigated by SEM. The images of SEM is shown in Figure 2. Images result for the SEM revealed the surface of the adsorbent is very irregular and porous. These type of the surface are good for absorbing heavy metal ions [4][10]. These images also can be deduced that many porous sites provides abundant active sites for adsorbing not only Cr but also for reducing COD, BOD, turbidity, TSS, color and pH.



(a) (b)

Figure 2. SEM Images of Adsorbent with Ratio 3:2 (a) 50 X (b) 100 X

3.4. Effect of Adsorbent Dose and Contact Time

To determine adsorption capacity and the contact time of activated sludge-zeolite adsorbent to adsorb heavy metal, experiment was conducted by putting the adsorbent with ratio 3:2 in dye solution with initial concentration of Cr at 70 mg/l. The removal efficiency was calculated by increasing the mass of adsorbent during the experiment. The result is shown in Figure 3 (a). The removal efficiency of Cr were 99.1, 85.1, and 56.5% in the adsorbent amount by 20, 15 and 10g. The increasing of adsorption percentage is equivalent with the increasing the mass of activated sludge–zeolite adsorbent because the increase of specific surface area and functional group of adsorbents is increased too.

The relationship between the contact time and the Cr concentration adsorption is shown in Figure 3 (b). The Figure 3(b) shows that the adsorption of Cr increased significantly at first 30 min then adsorption rate increased slowly at the remaining time until equilibrium condition. Increasing adsorption rate at first 30 min is caused by the adsorption sites were still vacant in the beginning, therefore adsorbates occupied easily to the sites.

When the time was increased, the vacant sites of adsorbent decreased gradually so that adsorption rate of Cr increase slowly until equilibrium condition. The equilibrium condition was found at 120 min with 0.3468 mg/g Cr adsorbed. The previous result reported that the equilibrium of Cr adsorption by novel green nanocomposite was reached at 80 min [16]. The difference between this result and previous result can be caused by the characteristic of the adsorbent and specific surface area of the adsorbent.

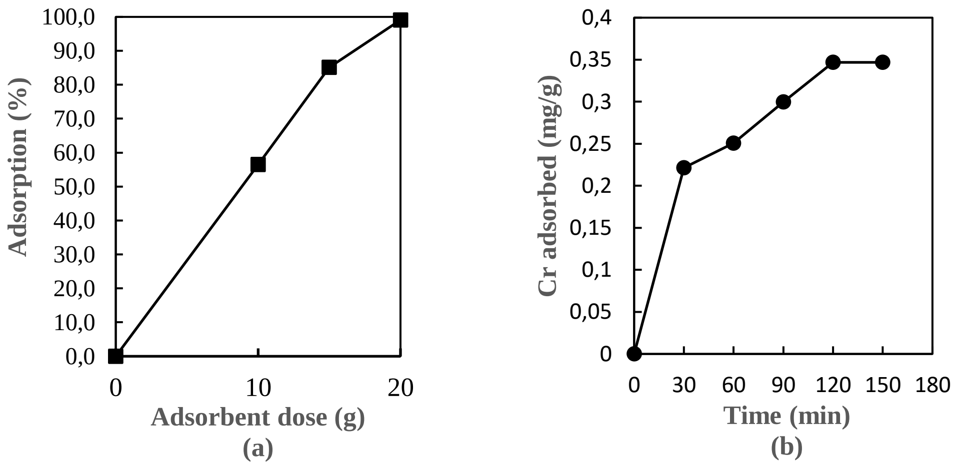


Figure 3. Effect of (a) Adsorbent Dose and (b) Contact Time

3.5. Adsorption of Dye Solution

Adsorption experiment was conducted by contacting activated sludge-zeolite adsorbent at ratio 3:2 with dye solution from Lampung ethnic textile industry. The results of adsorption of dye solution is shown in Table 2. Based on the result, activated sludge-zeolite adsorbent was able to reduce waste parameters form dye solution below the quality standard but some parameters (COD, BOD, turbidity, color, pH and TSS) was still above the quality standard. One of parameter which successfully decreased was Cr concentration. Activated sludge-zeolite adsorbent reduced Cr concentration from 70 to 0.63 mg/L.

Equilibrium adsorption of adsorbent was 0.346 mg/g. Despite the maximum adsorption capacity of heavy metal by activated sludge-zeolite was still lower than with modified *Peganumharmala* seed (53.48 mg/g) [16] and activated sludge for removing polyacrylate (399, 434 and 454 mg/g) [8], the result of reduction the concentration of heavy metal after adsorption was below the environmental quality standard (1 mg/L). Activated sludge-zeolite adsorbent also could reduce the other parameters of dye solution such as COD, BOD, turbidity, color, pH and TSS, however, the result of reduction were still above the environmental quality standard.

Table 2. Adsorption of Dye Solution with Activated Sludge-Zeolite Ratio 3:2

Parameter	Before adsorption	After adsorption	Quality standard	unit
Total Cr	70	0,63	1	mg/L
Total Cd	0.007	-	1	mg/L
Total Pb	0.0002	-	1	mg/L
COD	63.600	8195	150	mg/L
BOD	36.485	60	60	mg/L
TSS	1.620	132	50	mg/L
Color	83.750	25.600	50	Pt-Co
Turbidity	589	308	25	NTU
pH	11	8.5	6.0-9.0	

3.6. Adsorption Kinetics

Kinetic models of pseudo–first order and pseudo-second order were applied to investigate kinetic of Cr onto activated sludge-zeolite adsorbent.

Pseudo-first order model is

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

Pseudo-second order model is

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

Where q_e (mg/g) is the equilibrium adsorption amount of Cr, q_t (mg/g) is the adsorption amount of Cr at time t, k_1 (1/min) and k_2 (g/(mg.min)) are the constants of pseudo-first order and pseudo-second order.

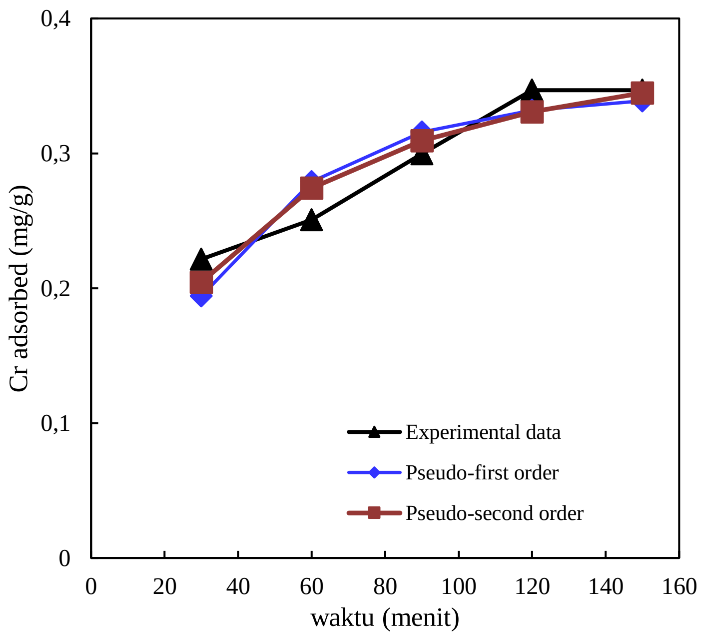


Figure 4. Pseudo-First Order and Pseudo-Second Order Kinetic Model

Table 3. Pseudo – First Order, Pseudo Second Order Kinetic Model for Cr Adsorption onto Activated Sludge – Zeolite Adsorbent

Kinetic model	Parameter	Value
Pseudo-first order	k_1 (min^{-1})	0.0277
	Predicted q_e($mg.g^{-1}$)	0.3443
	Experimental q_e($mg.g^{-1}$)	0.346
	SSE	0.0021
Pseudo-second order	k_1 ($g.mg^{-1}.min^{-1}$)	0.0774
	Predicted q_e($mg.g^{-1}$)	0.4162
	Experimental q_e($mg.g^{-1}$)	0.346
	SSE	0.0012

These models were used to fit experimental data and the results are shown in Figure 4 and Table 3. From the results, the pseudo-first order sum square error (SSE) was 0.0021, whereas the pseudo-second order SSE was 0.0012. For this calculation shows that experimental data is compliance with the pseudo-second model in terms of lower SSE. However predicted q_e from the pseudo-first model were more consistent with q_e from experiment than q_e calculation from the pseudo-second order. The pseudo-first order model describes a physical adsorption of Cr in dye solution onto activated sludge-zeolite adsorbent. The previous research shows that adsorption of textile dye kinetic model onto coconut shell activated carbon was consistent with pseudo-first order model in terms of consistency between calculated q_e and experimental q_e[1]. The other research found that adsorption of chromium was better to modeled with the pseudo-first order [17].

3.7. Isotherm Adsorption

The adsorption isotherm shows how the adsorbate interact with the adsorbent [18]. The interaction can be modeled using Langmuir and Freundlich. The linier form of these equations are as follow:

Langmuir

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

Freundlich

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \quad (5)$$

Where q_e is the amount of Cr adsorbed on the adsorbent (mg/g) at equilibrium, Ce the equilibrium of Cr in solution (mg/L), q_{max} the maximum adsorption amount for the adsorbent (mg/g), K_L Langmuir adsorption constant (L/mg), while K_F and n are Freundlich adsorption constants.

The Langmuir isotherm model has the essential characteristic to expresses adsorption process. It is called as the Langmuir equilibrium parameter R_L, R_L equation is as follow:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (6)$$

Where RL indicates the isotherms to be unfavorable (R_L>1), linier (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0) [18].

The experimental data were fitted by linearized Langmuir equation (Figure 5 (a)) and linearized Freundlich (Figure 5 (b)) equation. The constants of both equations are shown in Table 4. Based on the result from Table 4, the correlation coefficient (R^2) in the Langmuir model was higher than R^2 in the Freundlich model. Therefore, the Langmuir model was more suitable to represent adsorption isotherm of Cr onto activated sludge-zeolite adsorbent than The Freundlich model. The Langmuir model indicates that the adsorption process takes place at a homogenous sites and it also depicts the adsorption process is monolayer adsorption.

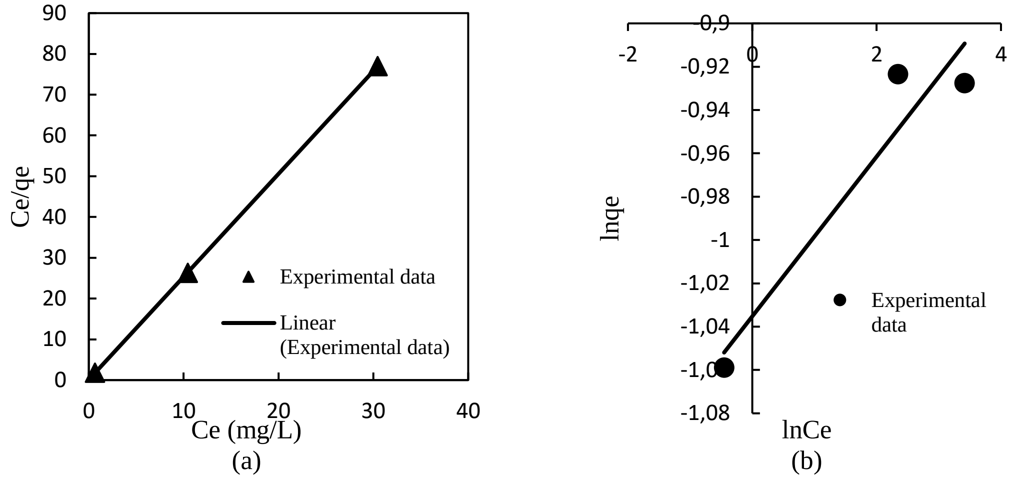


Figure 5. The Langmuir (a) and The Freundlich (b) Adsorption Isotherm

Table 4. Isotherm Parameter Coefficient for Adsorption of Cr in Dye Solution onto Activated Sludge-Zeolite Adsorbent

Isotherm parameters	**Value**
Langmuir	
q_{max} (mg/g)	0.3964
K_L (L/mg)	21.5256
R^2	1
R_L	0.000663
Freundlich	
K_F (L/g)	0.3553
n	27.1
R^2	0.9137

4. Conclusion

Adsorbent from mixing activated sludge from rubber industry and activated zeolite has been successfully in removing Cr in dye solution waste from Lampung ethnic textile industry. Another waste parameters was also reduced but still above the environmental quality standard. The highest value of BET surface area and pore diameter are obtained from ratio 3:2 (activated sludge and zeolite). The value of BET surface area, pore diameter and pore volume from adsorbent with ratio 3:2 are 923 m^2/g, 258.872 Å and 0.6 cm^3/g respectively. FT-IR results show that adsorbent with ratio 3:2 contains carboxyl group which has capacity to absorb heavy metal. The result of adsorption experiment showed that activated sludge-zeolite adsorbent could remove Cr contained in dye solution in about 99.1% within 120 min. Kinetic data followed the pseudo-first order kinetic model with k_1 is 0.0277 min^{-1}. The Langmuir adsorption isotherm model is fitted well to the experimental data with predicted q_{max} is 0.3964 mg/g.

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