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Kinetic Study of Removal of Congo Red and Direct Green

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Abstract. The pillarization process of Al/Fe metal oxide compound in bentonite has been carried. The study of weight adsorbent, pH, adsorption time, concentration and temperature adsorption were investigated to get the optimum condition of Congo red and Direct green removal. In addition, the pseudo kinetic and isotherm model were also determined to investigate the rate and type of adsorption. From the experiment, the optimum weight of adsorbent, pH, adsorption time, concentration and temperature were 0.3 g, 2, 45 minute, 90 mg/L, respectively. Thus, the pseudo kinetic model follow the pseudo second order while the Freundlich model was use as the isotherm model. As conclusion, The Pillarization success to enhance the adsorption capacity of bentonite to remove the Congo red and Direct green dyes.

1. Introduction

The layered material based on its existence is divided into layered material found in nature and synthesized. One example of layered material found in nature is bentonite. Bentonite has the chemical formula $(Mg, Ca) XAl_2O_3 \cdot ySiO_2 \cdot nH_2O$ with n values of about 8 and x, y is comparative values between Al_2O_3 and SiO_2 . Bentonite has a sheet structure (smectite). Each bentonite sheet consists of two tetrahedral layers arranged by the main element Si (O, OH) and flanking an octahedral layer composed of aluminium (Al), magnesium (Mg), and iron (Fe) elements [1].

Bentonite is modified in order to enlarge the distance between layers so that it can be effectively used as an adsorbent. Bentonite modification is done by process macro anion pillarization. The macro anion used is the Al/Fe metal oxide compound. The method of pillarization used in bentonite is the ion exchange method. When the macro anion pillared into bentonite layer, it will change the anion OH⁻ of bentonite which is mean at layer expected to increase the distance between the layers of bentonite [2].

Pillared bentonite Al/Fe is applied as a Congo red and Direct green. The Congo red substance has a red azo (RN = NR) group having the name IUPAC as a 1-naphthalene sulfonic acid, 3,4-bis biphenylenebis (azo) bis (4 aminodisodium). Congo red is toxic and difficult to be deregulated because it has a complex chemical structure and the presence of aromatic rings [3].

In this study, the adsorption process of Congo red by pillared bentonite metal oxide Al/Fe is intended to determine the effect of pH, adsorbent weight, contact time, concentration and temperature on the adsorption rates parameters by measuring residual concentration and adsorbed amount using UV-Vis Spectrophotometer. The pseudo kinetic and isotherm model were also investigated.



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2. Materials and Method

2.1 Materials

Bentonite clay was supplied from bentonite deposit located in Lampung Province, Indonesia. The Congo red and Direct green dye were obtained from the local market in Palembang, Indonesia. HCl and NaOH as pH adjusted of the dye solution were purchased from Merck Millipore in analytical grade and used as received without further purification.

2.2 Pillarization of Bentonite with Metal Oxides Al/

Al/Fe pillared bentonite was first synthesized by preparing a 1% bentonite suspension by adding 12 g of bentonite to 120 mL of distilled water for 2 hours. The prepared bentonite suspension was then added a solution of Al/Fe. The mixture is then distilled for 24 hours at room temperature. The formed solid is dried at 100°C, and then calcination is done using furnace with temperature 400°C for 2 hours.

2.3 Effects of Adsorbent Weight

50 mL of Congo red and Direct green dye solution with concentration of 100 mg/L in interaction with bentonite polarized Al/Fe metal oxide and natural bentonite (control) with variation of weight of adsorbent 0.03; 0.05; 0.1; 0.2 and 0.3 g. The mixture was stirred using a horizontal shaker for 60 minutes, then the dyestuff solution having been centrifuged and measured using UV-Vis Spectrophotometer.

2.4 Effect of pH

The effect of pH was studied by interaction of 0.05 g bentonite which had been polarized by Al/Fe metal oxide and natural bentonite (control) and then added to 50 mL of Congo red and Direct green dye with concentration of 100 mg/L while stirring in a horizontally using shaker within 1 hour. pH was adjusted by 0.01 M HCl or 0.01 M. NaOH. The pH variations used were 1, 2, 3, 4, 5 and 6. Then we observed the stability using UV-Vis spectrophotometer.

2.5 Effect of Timer Adsorption and Kinetic Parameters

A total of 0.05 g of natural bentonite (control) was added to 5 mL of dye with a concentration of 100 mg/L. The mixture is stirred with a horizontal shaker at predetermined intervals. Adsorption time variation starts from 5, 10, 15, 20, 30, 45, 60 and 120 minutes. Pigment which has gone through the adsorption process is separated and measured its absorbance using a UV-Vis spectrophotometer. The same procedure is performed for the pillarized bentonite adsorbent. The amount of residual concentration (C_e) and the amount of adsorbed dye ($Co-C_e$) was calculated using the standard solution calibration curve equation, while the kinetic model can be calculated using pseudo first order and second order pseudo equation [4].

3 Effect of Concentration, Temperature and isotherm model

The effect of thermodynamic adsorption of the dyestuff by the natural bentonite (control) and the alkylated bentonite of the Al/Fe metal oxide compound is carried out through a series of experiments by varying the concentration of dye and the adsorption temperature. A total of 0.05 g of natural bentonite adsorbent (control) was mixed with 50 mL of dye at concentration 20, 40, 50, 70 and 90 mg/L. Adsorbents that have been mixed with dyestuffs are stirred using a horizontal shaker for 1 hours at temperatures varying by 30, 50 and 70°C. The mixture was separated, and then the dye solution separated from the adsorbent measured the absorbance value using a UV-Vis spectrophotometer to determine the residual dyestuff concentration after the adsorption process. The same procedure is performed for the alpha / metallized atomized bentonite adsorbent. To find out the applicable adsorption isotherm model used Langmuir and Freundlich equations [5].

3. Results and Discussion

3.1 Effect of Adsorbent Weight

Variation of adsorbent weight was conducted in order to know the influence of adsorption weight between natural and pillared bentonite as presented in figure 1.

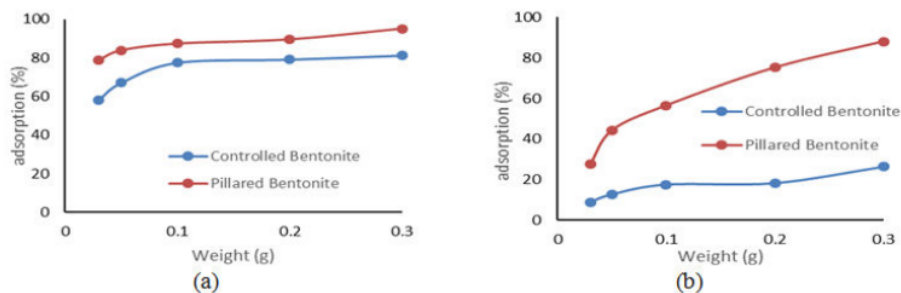


Figure 1. Effect of adsorbent weight on: (a) Congo red and (b) Direct green

Figure 1a shows the adsorption of Congo red dye rising as the increasing the adsorbent weight. It is due to the availability of the active side on the bentonite surface [6]. From the figure 1a shows for both adsorbents at a weight of 0.03 to 0.3 g an increase in the absorption percentage of the dye applies. Vice versa at a weight of 0.1 to 0.3 g, it is indicated the adsorbed concentration of Congo red is not much different so that the optimum weight of the weight variation is 0.3 g. At the figure 1b, the adsorption of Direct green dye higher than the congo red dyes. It is assumed due to the availability of the active side on the bentonite surface [7]. The figure shows the natural and pillared bentonite for all concentration variation Direct green adsorbed increasingly so we can obtain the optimum weight on the weight variation of 0.3 g.

3.2 Effect of Initial pH

Effect of pH on natural and pillared bentonite to Congo red and Direct green removal are presented in figure 2.

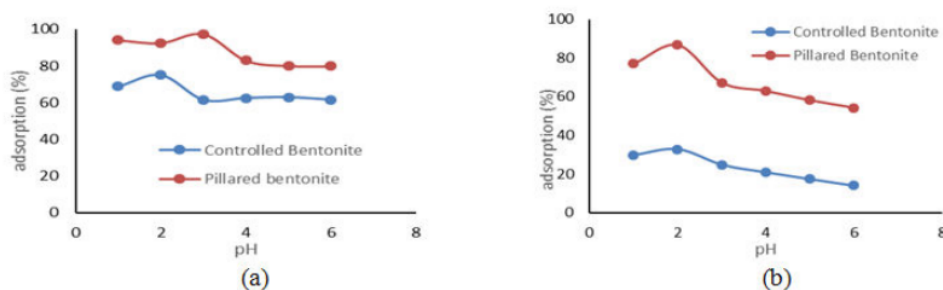


Figure 2. Effect of pH on: (a) Congo red and (b) Direct green

Natural bentonite has an optimal pH at pH 3 with an adsorbed percentage of 75.14%. In other side, the pillared bentonite has an adsorbed percentage of 97.36 %. When refer to the pH pzc of pillared bentonite i.e. pH 4, Congo red which is anionic (-) will tend to be interested in cationic (+), this means Congo red will be more absorbed below 4 [8]. The evident in Fig. 2, there is an increase of Congo red adsorption pH below the pH pzc 3. Natural bentonite has an optimal pH at pH 2 with the percentage adsorbed of 32.78%. Pillared bentonite of Al/Fe metal oxide has an optimum pH at pH 2 with an

adsorbed percentage of 86.72%. When refer to the pH pzc of pillared bentonite i.e. pH 4 , Congo red which is anionic (-) will tend to be interested in cationic (+), this means Congo red will be more absorbed below 4. The evident in Fig. 2 shows an increase in direct adsorption of the green below pH 2 pH pzc.

3.3 Effect of Adsorption Time

The effect of adsorption on the removal of Congo red and Direct green using natural and pillared bentonite are shown in figure 3.

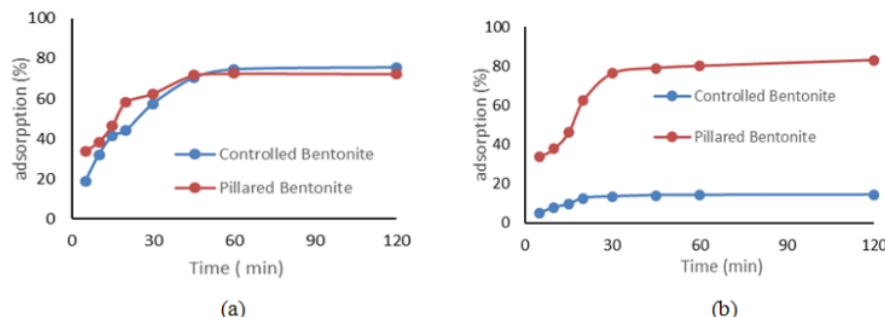


Figure 3. Effect of adsorption time on: (a) the Congo red and (b) Direct green

In figure 3a, both adsorbent have the similar capacity to absorb the adsorbate. In the figure, the optimum adsorption time is on 45 minutes and the amount of Congo red removal as much as 76.21%. Therefore for the Direct green adsorption (figure 3b), both adsorbent only need shorter time to reach the optimum time i.e. 30 minutes. Contrary to the Congo red removal, the capacity adsorption of both adsorbent has significant differences. The pillared bentonite can remove until 80% while the natural bentonite only maximum 12.61 %. It is shown that the pillared bentonite suitable for absorbing the Direct green dyes. The adsorption capacity is dependent on contact time, the longer contact time between the dye and composite increases the adsorption capacity [9]. The adsorption kinetics study is an important factor to evaluate the rate of dye removed by the adsorbent. This uses data derived from the contact time by entering into the pseudo-first order and second order formula. The natural bentonite has a smaller adsorption rate than pillared. It is caused the Al/Fe metal oxide give a greater reactive rate as listed in Table 1.

Table 1. Constant of kinetic adsorption model of Congo red and Direct green

Type of Adsorbate(Adsorbent)	Experimental Qe	Pseudo-first-order (PFO)		Pseudo-Seconds-order (PSO)	
		Qe	R ²	Qe	R ²
CR (Natural bentonite)	75.55	105.43	0.9246	87.37	0.9868
CR (Pillared bentonite)	77.69	85.50	0.9296	85.61	0.9961
DG (Natural bentonite)	14.2811	12.0466	0.966	15.4301	0.9949
DG (Pillared bentonite)	47.4601	65.4476	0.9455	54.7895	0.9872

From the Table 1 shows the adsorption of phenol on activated bentonite match with the PSO kinetic adsorption model because the correlation coefficient (R²) of PSO is the higher than the PFO. In addition, The Qe value of PSO order quite similar to the Qe from experimental [10]. This result indicates that the adsorption process follows PSO kinetics.

3.4 Effect of Adsorption Concentration and Temperature

The efficiency of Congo red and Direct green removal by natural and pillared bentonite are shown in figure 4.

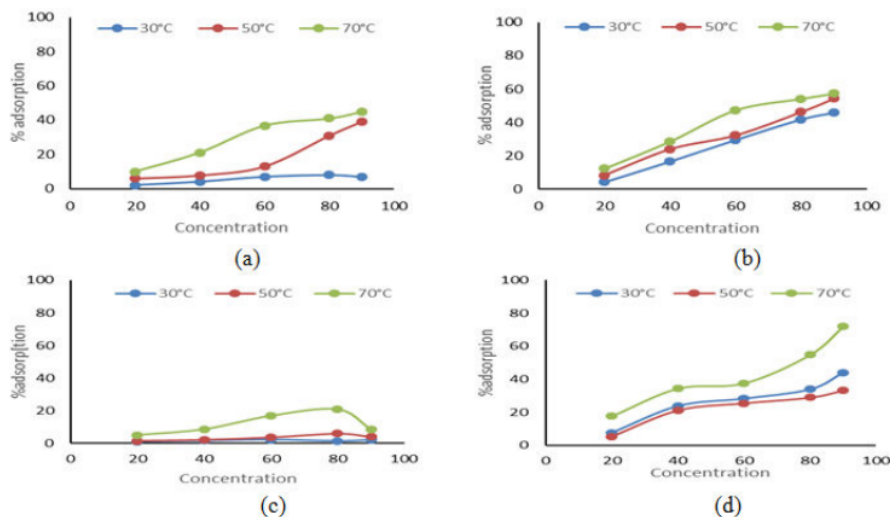


Figure 4. Effect of concentration and temperature on Congo red by: (a) natural bentonite and (b) pillared bentonite; and Direct green by: (c) natural bentonite and (d) pillared bentonite

Figure 4a and b shows that increasing the adsorption temperature and concentration causes the amount of adsorbed Congo red was also increased. This is because when the temperature increases the collision between adsorbent molecules with adsorbate molecules are faster so that the Congo red dye pushed into the layers of natural bentonite and pillared bentonite, thus causing the concentration of absorbed increased [11]. Furthermore, figure 5c and d shows for the natural bentonite, the pores of the adsorbent have not opened too large so when adsorbate absorbs on the surface of the adsorbent it will cause the closure of the pores even when the temperature was raised. Conversely, the pore of the pillared bentonite had opened up to the maximum so they can absorbed the mixture optimally [12]. The adsorption process was calculated based on adsorption isotherm parameter using Langmuir and Freundlich equation. The Langmuir isotherm model can explain the adsorption process on the adsorbent occurring on the surface of the adsorbent and adsorption occurred monolayer, while the Freundlich adsorption isotherm model can be used to predict the adsorption capacity of the adsorbent. The following isotherm adsorption data is displayed on Table 2. From the data presented in Table 2, the adsorption isotherms using the Freundlich model have better adsorption data than the Langmuir model. The correlation coefficient (R^2) Freundlich models have higher values than the model of Langmuir. This shows that in adsorption of Congo red and Direct green dye adsorbents using natural and pillared bentonite is more suitable to use Freundlich adsorption isotherm model.

Table 2. The coefficient correlation of adsorption isotherm model on Congo red and Direct green adsorption

Tempe Rapture (°C)	Congo red				Direct green			
	Freundlich		Langmuir		Freundlich		Langmuir	
	NB	PB	NB	PB	NB	PB	NB	PB
30	0.9294	0.9504	0.2563	0.6532	0.3724	0.9417	0.1002	0.1365
50	0.8676	0.9059	0.076	0.439	0.8501	0.9845	0.1574	0.998
70	0.9498	0.7327	0.0274	0.0643	0.7518	0.8547	0.02559	0.7844

4. Conclusions

The adsorption capacity of bentonite was successfully enhance by modification using Al/Fe metal to pillar the inner layer of bentonite. Congo red and Direct green dye can be adsorbed by natural bentonite and Al/Fe pillared bentonite. The results showed that the adsorption of Congo red and Direct green on raw natural and pillared bentonite followed the pseudo-second-order kinetic and Freundlich isotherm model.

Acknowledgments

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