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Abstract

Study of doping process of metal oxide Cr(III) onto bentonite for phenol removal has been done. The purpose of this study was to increase the capacity and effectiveness of bentonite adsorption. The doped bentonite was characterized using XRD, SEM-EDX and FT-IR spectrophotometer analysis. XRD characterization result showed an angle shift (2θ) characteristic at 1.609° . The SEM-EDX characterization result showed that bentonite as control have a more gaps than Cr(III)-doped bentonite. Based on EDX result, the Al element decreased from 7.53% to 3.76%, Si from 19.84% to 10.23% and appeared Cr element 2.06%. The FT-IR characterization result showed no significant friction in the spectrum so it can be identified as physical adsorption. The adsorption of phenol was applied at pH_{pzc} , which for bentonite as control was applied at pH 4 and Cr(III)-doped bentonite was applied at pH 8. The phenol adsorption rate fitted to pseudo-second-order and it was found that the equilibrium data was best followed by Freundlich isotherm model, the amount of adsorption rate constant (k) and adsorption capacity (Q_e) was $0.0024 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ and 16.95 mg/g . The Enthalpy (ΔH) and entropy (ΔS) values decrease with increasing phenol concentration and the positive free energy value was indicated that the process was nonspontaneous because there has been an equilibrium state. Based on the adsorption result, it can be concluded that the doping method can produce better bentonite performance to adsorb phenol.

Keywords: adsorption, phenol, bentonite, Cr (III), doping

Introduction

One of the most compounds commonly found in waste is phenol. It has its presence in the effluent from major chemical and pharmaceutical industries such as petrochemical industries, petroleum refineries, coal gasification operations, a liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent. Phenol causes harmful side effects such as sour mouth, diarrhea, impaired vision, excretion of dark urine. Phenol is considered as one of the priority pollutants owing to its danger to organisms at low concentration. It is also toxic for fishes [1]. Environmental Protection Agency regulations call for lowering of phenol content in wastewater to less than 1 ppm. Adsorption is a surface phenomenon with a common mechanism for organic and inorganic pollutants removal [2]. Adsorbents that can remove phenol were zeolite [3], activated carbon [4] and bentonite [5]. Recently, many

researchers have been using natural materials like bentonite and modified bentonite for removal phenol.

According to Said [6], they found the adsorption is a promising method for phenol removal. One of the adsorbents used for phenol adsorption was bentonite. Bentonite is a layered material or clay containing inorganic minerals found in nature [7]. It is a three-layered clay mineral composed of silica and alumina. Its layers are not electrically neutral and have a negative charge. To overcome the electrical repulsion due to it, the negative charge is established between the layers and a series of positively charged cations fall between that layer. One of the methods for the activation of natural bentonite is activation by strong mineral acids. As a result of contact between montmorillonite and strong mineral acid like sulfuric acid, inter-layers cations are separated and proton is substituted. Activated bentonite is able to degrade a range of water contaminants and industrial wastewater [Liu and Zhang]. The abundance of bentonite

in most continent of the world and it is low cost make it strong candidate as an adsorbent for the removal of many pollutants from wastewater like phenol. The choice of bentonite because it has several advantages such as high porosity level and easy to find and can be modified in the laboratory [8]. Chidi *et al.* [9] was investigated the potential of bentonite to absorb phenols from aqueous solutions. From the previous studies, the ability of bentonite has not been maximized in absorbing phenol therefore the researcher did a modification onto the surface and into the layer of bentonite. Compounds that will be doped onto bentonite in the form of Cr(III) will have a good adsorption activity and unique morphology [10]. Chromium was chosen because it can be tracked spectroscopically [11]. The chrom used in the form of Cr (III) can easily can be doped on the surface of bentonite. Therefore, Cr (III)- doped onto bentonite has a high adsorption ability, because Cr can enter the bentonite surface and form complexes with phenolic anion compound.

In this research, bentonite and Cr(III) compounds would be doped. The objective of this research to determine the optimum condition of phenol removal. Bentonite doped with Cr(III) compound will then be characterized using FT-IR spectrophotometer, SEM-EDX, and XRD. In its application, optimal bentonite doped by Cr(III) compounds was expected to be an adsorbent to adsorb phenol. The adsorption parameters tested included: kinetic parameters (adsorption rate), isotherm (Langmuir and Freundlich constants), and thermodynamics (enthalpy, entropy and Gibbs free energy) to determine the residual concentration (mg/L) and the amount of phenol adsorbed (mg/L) by activated (control) bentonite and bentonite doped by Cr(III) compounds, then a UV-VIS spectrophotometer was analyzed. It was hoped that after this research will be carried out the material that can adsorb phenol optimally.

Materials and Methods

Materials. The materials used in this study were natural bentonite from PT. Indonesian Natural Bentonite, phenol (C₆H₅OH), sulfuric acid (H₂SO₄), distilled water (H₂O), sodium hydroxide (NaOH) 0.5 M, and hydrochloric acid (HCl) 0.5 M, chromium(III) chloride hexahydrate (CrCl₃.6H₂O) 0.5 M, Folincioalteau, sodium chloride (NaCl) 0.01 M, and sodium carbonate (Na₂CO₃) 20%, all chemicals were provided from Merck.

Preparations and activations of bentonite. A total of 50 grams of natural bentonite added 500 mL of distilled water mixed in 1000 mL beaker and stirred for 24 hours. The mixture was acidified with 250 mL of 2M sulfuric acid and distilled for 10 hours at 65 °C. The suspension formed was left to settle and washed repeatedly with distilled water until the pH solution is around 5 and centrifuged at 4000 rpm for 10 minutes. After that, the solid

was dried in an oven with a temperature of 100 °C for 10 hours then bentonite was crushed and sieved with a 200 mesh sieve. Then the prepared bentonite was called activated bentonite. Activated bentonites were characterized using FT-IR spectrophotometers, SEM-EDS and XRD.

Preparation of Cr(III) doping solution. A 100 mL of CrCl₃.6H₂O 0.5 M was put into a glass cup; and dripped slowly with 400 mL of NaOH 0.5 M. After that the distillation solution at 4000 rpm for 24 hours was then allowed to stand for 2 days at room temperature and obtained Cr(III) doping solution.

Process of Cr(III) doped bentonite. as many as 24 grams of activated bentonite are put into 240 mL of distilled water and distilled for 2 hours until the clumps of clay are lost. Then the Cr (III) doping solution was added to the bentonite mixture. The mixture of Cr(III)-bentonite was then dried in an oven at a temperature of 100 °C for 2 hours. The resulting composites were then characterized using FTIR, SEM-EDS, and XRD.

Effect of adsorption time and kinetic parameters. A total of 0.05 g of activated bentonite (control) adsorbent was added to 30 mL phenol with a concentration of 100 mg/L. The mixture was stirred with the horizontal shaker at a predetermined time interval. The time variation of adsorption starts from 20, 30, 40, 50, 60, 70, 80 and 90 minutes. Phenol was filtered, diluted 10 times and measured its absorbance using a UV-VIS spectrophotometer. The same procedure is carried out for doping bentonite adsorbents. The remaining concentration (mg/L), the amount of adsorbed phenol (mg/L) was calculated using the standard solution calibration curve equation, while the adsorption rate (k_1) and (k_2) can be calculated using pseudo-first-order and pseudo-second-order equations.

Effect of concentration, temperature, isotherm and thermodynamic parameters. The isotherm and thermodynamic parameters of phenol adsorption by activated (control) bentonite and Cr (III) doped bentonite were carried out through a series of experiments by varying phenol concentration and adsorption temperature. A total of 0.05 g of adsorbent of activated bentonite (control) were mixed with 50 mL of phenol (25, 50, 75, 100 and 150 mg/L). The phenol with the various concentration was heated using a hotplate with the various temperature (30, 40, 50, 60 and 70 °C), and then the adsorbent was transferred into each phenol solution, the adsorbent mixed with phenol was stirred using a horizontal shaker for 80 minutes. The mixture was separated, then the phenol solution which had been separated from the adsorbent was diluted 10 times and measured the absorbance value using a UV-Vis spectrophotometer to determine the concentration of the remaining phenol after the adsorption process. The same procedure was performed for Cr(III) doped bentonite. Therefore, the

thermodynamic parameters in the form of enthalpy, entropy, and Gibbs free.

The thermodynamic parameters are determined using the equation:

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \quad (1)$$

$$E = -RT \ln K \quad (2)$$

Information:

C= Adsorbate residual concentration (M)

K = equilibrium constant

b = adsorption capacity (mol / g)

m= mol of adsorbate (mol)

E = energy of adsorption (kJ / mol)

R = gas constant (J/mol.K)

T = Temperature (K)

Meanwhile, to find the value of the enthalpy and entropy, the following equation is used:

$$\ln Kd = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (3)$$

Information :

Kd = adsorbate distribution coefficient (q_e / C_e)

ΔH = Enthalpy (J)

ΔS = Entropy (J)

R = Constant (J/mol.K)

T = Temperature (K)

Results and Discussion

Characterization of bentonite as control and Cr(III)-doped bentonite using XRD. Firstly, the Controlled Bentonite was activated to remove impurities using acidification with the addition of sulfuric acid (H_2SO_4). This acidification serves to remove small metals as impurities attached to bentonite. This is due to the metals contained in the bentonite bound to H^+ ions originating from acid, so the layer will be more open.

Bentonite control and doped metal oxide Cr(III) were then characterized using XRD. The characterization using XRD aims to see the changes that occur in the control bentonite (activated) into bentonite doped with metal oxide Cr(III). The results of XRD characterization are shown in Figure 1. From the results of XRD characterization data, it can be concluded that the diffraction angle shift (2θ) which is the diffraction angle (2θ) of bentonite of 5.671° shifts to the diffraction angle of 7.28° which indicates the presence of other cations in the form of Cr(III) in the bentonite plane [12] Figure 1(b). shows many peaks with high intensity between at the diffraction angle (2θ) 45.425° which is a typical angle of Cr_2O_3 (JCPDS card no. 70-3766) [13].

Characterization of bentonite as control and Cr(III)-doped bentonite using FT-IR spectrophotometer. The results of FT-IR characterization of control bentonite and

Cr (III) doping as well as those absorbed by phenol can be seen in Figure 2.

The FT-IR spectrum of control bentonite can be seen in Figure 2(a) which shows the stretching vibration of Al-OH-Al at wave number 3645.46 cm^{-1} and vibration of bending Al-OH-Al at wave number 921.97 cm^{-1} . H-O-H stretching vibration was observed at wave number 3211.48 cm^{-1} while the bending vibration H-O-H appeared at wave number 1614.42 cm^{-1} . The appearance of strong absorption at wave number 1112.93 cm^{-1} shows the stretching vibration of Si-O-Si [14].

The FT-IR spectrum of control bentonite that has absorbed phenol can be seen in Figure 2(b). In the spectrum shows the stretching vibration of Al-OH-Al at wave number 3643.53 cm^{-1} and vibration of bending Al-OH-Al at wave number 923.9 cm^{-1} . H-O-H stretching vibration was observed at wave number 3248.13 cm^{-1} while the bending vibration of H-O-H appeared at wave number 1633.71 cm^{-1} . The appearance of strong absorption at the wave number 1112.93 cm^{-1} shows the stretching vibration of Si-O-Si[15]

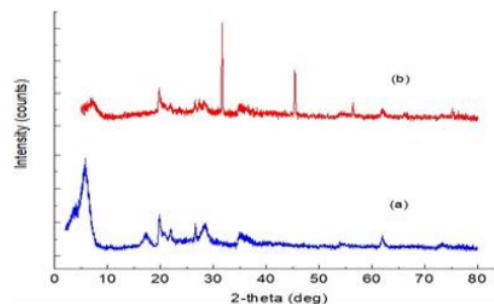


Figure 1. XRD Spectrum: (a) Controlled Bentonite (activated), (b) Cr (III) doped Bentonite

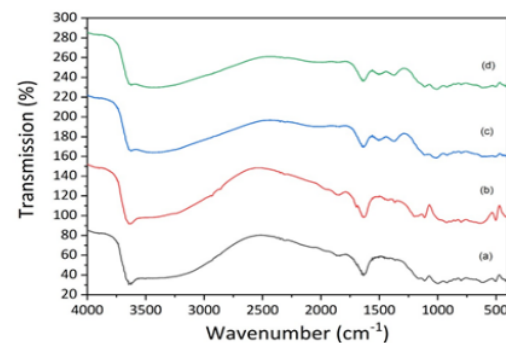


Figure 2. FT-IR Spectrum (a) Controlled Bentonite, (b) Con-trolled Bentonite Adsorb Phenol, (c) Cr(III) Doped Onto Bentonite, (d) Cr(III) Doped Onto Bentonite Adsorb Phenol

Figure 2(c) shows the spectrum of FT (IR) bentonite doped with Cr (III). From the spectrum shows the stretching vibration of Al-OH-Al at wave number 3624.25 cm^{-1} and bending vibration Al-OH-Al at wave number 920.5 cm^{-1} . H-O-H was observed at wave number 3246.2 cm^{-1} while the vibration of H-O-H appeared at wave number 1633.71 cm^{-1} . The appearance of strong absorption at the wave number 1112.93 cm^{-1} shows the stretching vibration of Si-O-Si. Cr-O vibrations appear at wave number 501.49 and vibration Cr = O at wave number 1010.7 which is characteristic of metal oxide Cr_2O_3 [16].

The FT-IR spectrum of Cr (III) doped bentonite which has absorbed phenol can be seen in Figure 2(d). From the spectrum shows that there is stretching Al-OH-Al vibration at wave number 3452.58 cm^{-1} and bending vibration Al-OH-Al at wave number 923.9 cm^{-1} . H-O-H stretching vibrations were observed at wave numbers 3232.7 cm^{-1} while the bending vibrations of H-O-H appeared at wave number 1633.71 cm^{-1} . The appearance of strong absorption at the wave number 1112.93 cm^{-1} shows the stretching vibration of Si-O-Si.

From the results of FT-IR characterization data it can be concluded that the adsorption that occurs is physical adsorption because the FT-IR spectrum before and after adsorbing phenol does not have a significant shift, whereas in the FT-IR spectrum the control bentonite and

bentonite doped by Cr (III) is found where Cr-O vibration appears at wave number 501.49 and vibration Cr = O at wave number 1010.7 which is characteristic of Cr_2O_3 in bentonite FT-IR spectrum doped so that it can be concluded that metal oxide Cr (III) successfully doped into bentonite.

Characterization of controlled bentonite (Activated) and Cr(III)-doped bentonite using SEM-EDX. In this research, SEM-EDX characterization was used to see the doping surface of bentonite with metal oxide Cr(III). SEM results can be seen in Figure 3. Figure 3(a) and (b) showing the results of the bentonite control analysis, while Figure 3(c) and (d) show the results of bentonite analysis that has been doped with Cr(III). In Figure 3(a) and (b) bentonite controls that still have many gaps, are different from Figure 3(c) and (d) which have been doped using Cr(III) oxide the surface is covered by Cr(III) so that the gap is reduced.

The EDX results can be seen in Table 1. The EDX results show that there is a decrease in the percentage of elements present in the control bentonite, especially the Al and Si elements which are located on montmorillonite which is the main constituent of the bentonite in which the dopants enter. However, with the presence of a dopant in the form of metal oxide Cr(III), the metal oxide will increase in percentage. The EDX spectra and component can be seen in Figure 4 and Tabel 1.

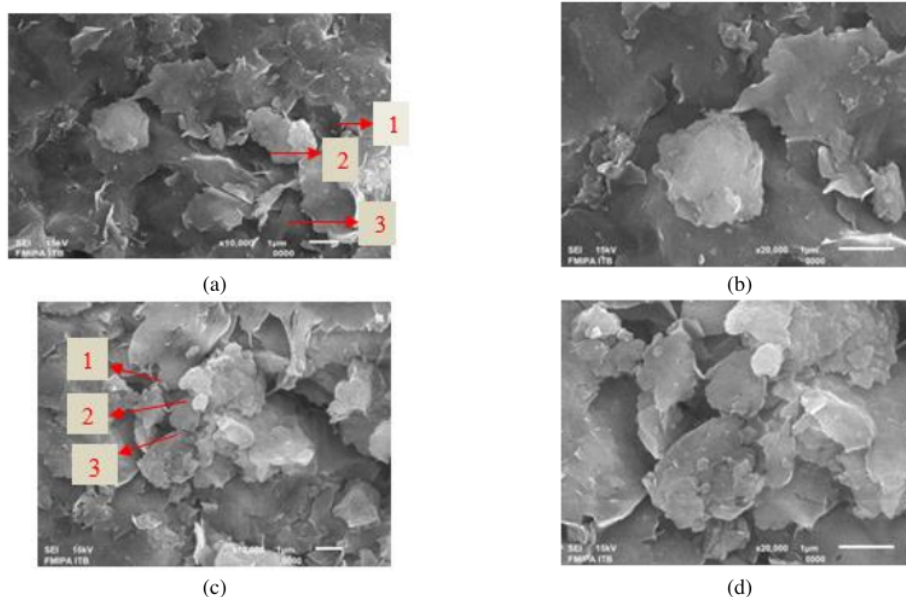


Figure 3. SEM Images: (a) 10.000x Zoom in of Controlled Bentonite, (b) 20.000x Zoom in of Controlled Bentonite, (c) 10.000x Zoom in Cr(III) Doped Onto Bentonite, (d) 20.000x Zoom in Cr(III) Doped Onto Bentonite

Table 1. The Results of Elemental Analysis using EDX

Element	Al (%)	Si (%)	Cr (%)
Controlled Bentonite	7.53	19.84	-
Cr(III) Doped Bentonite	3.76	10.23	2.06

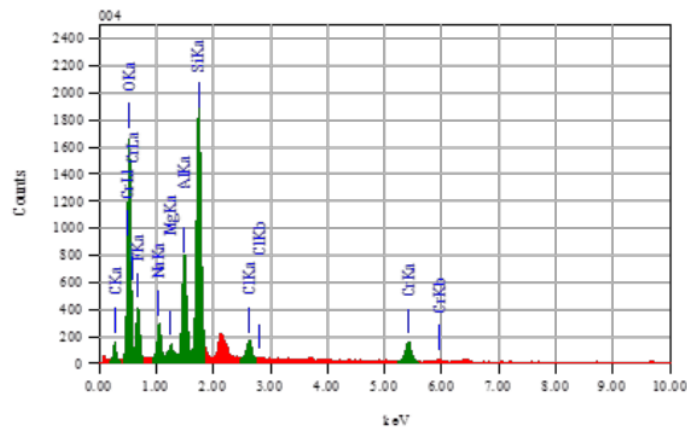
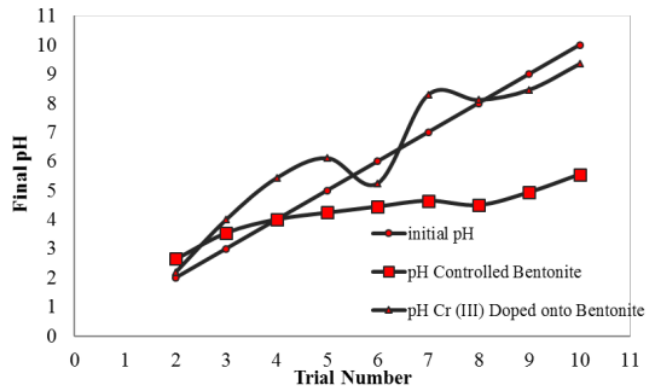


Figure 4. The Spectra of EDS Cr (III) Doped-bentonite

Figure 5. pH_{pzc} bentonite control and Cr(III) doped into bentonite against NaCl solution

From Table 1 it can be seen that there is a decrease in the percentage of Al elements to 3.76%, Si to 10.23% and the emergence of Cr elements of 2.06%. Therefore, it can be concluded from the results of SEM-EDX that Cr (III) oxide successfully doped onto bentonite.

Measurements of Point Zero Charge Controlled Bentonite and Cr(III) Doped onto Bentonite. The results of bentonite as control and Cr(III)-doped bentonite were analyzed by measuring pH Point Zero Charge (pH_{pzc}). Analysis of pH_{pzc} is the condition at a pH point

where the condition of the adsorbent surface has no charge. The purpose of this pH_{pzc} measurement is to determine the effect of pH on the surface content of bentonite. pH_{pzc} analysis was carried out using the pH drift method (shifting pH) as done by Fabriyanty *et al.* [17]. Data on the effect of pH_{pzc} on the adsorbent bentonite control and Cr (III) doped bentonite are shown in Figure 5.

Figure 5 shows the control bentonite and Cr (III) doped bentonite with pH_{pzc} which is the same as the initial pH

and final pH. In bentonite control pH_{pzc} 4 and bentonite doped on pH_{pzc} 8. According to [18], bentonite is an anionic clay or layered material which has a negative surface property, so that the pH below pH_{pzc} bentonite surface will be positively charged due to pH less than pH_{pzc} . Bentonite surface conditions have excessive H^+ .

Conversely on bentonite after doping with metal oxide Cr (III) has positive surface properties, so that at pH above pH_{pzc} surface of bentonite will be negatively charged because pH is more than pH_{pzc} the surface condition of the bentonite has OH^- excess. The effect of pH_{pzc} on phenol adsorption greatly affects the percentage of phenol adsorption. The results of pH_{pzc} analysis found that pH_{pzc} control bentonite compounds at pH 4 and bentonite doped Cr (III) were at pH 8.

Effect of Adsorption Time and Kinetic Parameters.

The effect of contact time of phenol adsorption by activated (control) bentonite and Cr (III) doped bentonite was carried out with phenol concentration of 100 mg/L. The adsorption process was carried out by stirring during the adsorption contact time which varied between 20, 30, 40, 50, 60, 70, 80 and 90 minutes. The graph of the effect of contact time on % adsorption can be seen in Figure 6.

In Figure 6 can be seen by increasing the adsorption time so that the adsorbed phenol will also increase. This is due to the longer the collision time between the adsorbent and the adsorbate, the more adsorbates are adsorbed by the adsorbent.

Figure 6 shows that Cr(III) doped bentonite can absorb more phenol than bentonite control. This is because Cr(III) doped bentonite has a larger surface area than the bentonite control so that it can absorb phenol more optimally [19]. From the graph of Figure 5 above, the control bentonite and bentonite doped with Cr(III) at 20 to 70 minutes experienced an increase in the adsorbed phenol concentration, but at 80 to 90 minutes the adsorbed phenol concentration was not much different, at 80 minutes the optimum time for the phenol adsorption process using natural bentonite adsorbent is 7.860% and Cr(III) doped bentonite is 21.930%.

Based on the adsorption time data, the adsorption rate can be calculated using pseudo-first-order and pseudo-second-order equations. The kinetic model of adsorption of phenol on the influence of time can be seen in Table 2.

Table 2. The Constants Kinetic of Phenol Adsorption

Adsorbent	$Q_{e\text{ exp}}$	Pseudo-first-order			Pseudo-second-order		
		Q_e	k_1	R^2	Q_e	k_2	R^2
Controlled Bentonite	4.828	9.246	0.0484	0.908	7.519	0.00271	0.972
Cr(III) doped Bentonite	13.228	30.27	0.0023	0.973	16.95	0.0024	0.992

From Table 2 shows that the adsorption capacity (Q_e) of bentonite control and Cr(III) doped bentonite to phenol has a pseudo-second-order equation value because it is closer to the experimental adsorption capacity value ($Q_{e\text{ exp}}$). Where the greater the order, the better the adsorption capacity [20]. The pseudo-second-order adsorption rate for phenol by Cr(III) doped adsorbent has a correlation coefficient (R^2) of 0.992 and a control bentonite of 0.972. The correlation coefficient value is higher than using the pseudo-first-order adsorption model which has a correlation coefficient (R^2) of 0.973 for Cr(III) doped bentonite and 0.908 for bentonite control. This shows that the pseudo-first-order and pseudo-second-order adsorption rate on Cr(III) doped bentonite is greater than the bentonite control so that the Cr(III) doped bentonite adsorbent has greater reactivity than the bentonite control before doping. The reaction rate for the bentonite control was 0.00271 and the reaction rate of Cr(III) doped bentonite was 0.0024.

Effect of Concentration and Temperature and Isotherm and Thermodynamic Parameters. The effect of concentration and temperature of phenol adsorption by controlled bentonite and Cr(III) doped bentonite can be seen in Figure 7 and 8.

Figure 7 shows the effect of temperature and phenol concentration on bentonite control and Figure 8 shows the effect of temperature and phenol concentration on Cr(III) doped bentonite. Where the temperature and

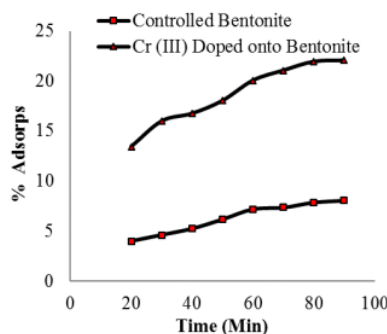


Figure 6. Effect of Phenol Adsorption Time using Controlled Bentonite and Cr(III) Doped Onto Bentonite

concentration of adsorption increases, the amount of adsorbed phenol also increases. This is because when the temperature increases collisions occur between the molecules of the adsorbent and adsorbate which are getting faster so that the phenol is pushed into the layers of the control bentonite and bentonite doped with Cr(III), which causes an increasing concentration of phenol adsorbed [21].

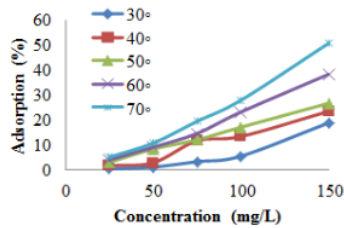


Figure 7. Effect of Phenol Concentration and Temperature on Controlled Bentonite

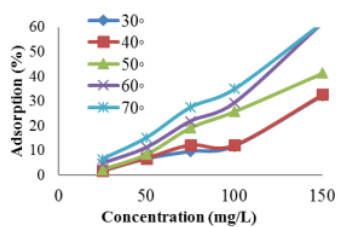


Figure 8. Effect of Phenol Concentration and Temperature on Cr(III) Doped Onto Bentonite

The adsorption process with the effect of phenol concentration at various temperatures was calculated based on the parameters of the adsorption isotherm using the Langmuir and Freundlich equations. The Langmuir adsorption isotherm model can explain the adsorption process on the adsorbent occurs on the surface of the adsorbent and adsorption takes place in a monolayer, while the Freundlich adsorption isotherm model describes the adsorption process to occur in a multilayer manner [22]. Data on adsorption isotherms using the Langmuir and Freundlich models can be seen in Tables 3 and 4.

From the data presented in Tables 3 and 4, the adsorption isotherm using the Freundlich model has better adsorption data than the Langmuir model. The correlation coefficient (R^2) of the Freundlich model has a higher value than the Langmuir model. This shows that in phenol adsorption using the control bentonite adsorbent and Cr(III) doped bentonite is more suitable using the Freundlich isotherm model where the adsorption process occurs in a multilayer manner.

The thermodynamic adsorption parameters which include Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for control bentonite and doped Cr(III) can be seen in Tables 5 and 6. From the calculation data of thermodynamic parameters (Gibbs free energy (ΔG), entropy (ΔS), enthalpy (ΔH)) presented in Table 5 shows the value of adsorption capacity increases with increasing temperature for the control bentonite adsorbent and Table 6 shows the value of adsorption capacity also increases with increasing temperature for Cr(III) doped bentonite adsorbent. Bentonite control adsorption capacity and doping Cr(III) also increased with increasing concentration.

Table 3. Data on Adsorption Isotherm Using the Langmuir Model

Temperature (°C)	Parameter	Unit	Controlled Bentonite	Cr(III)Doped Bentonite
30	K_L	L/mg	0.0077	0.0064
	Q_m	mg/g	1.0256	6.711
	R^2	-	0.887	0.639
40	K_L	L/mg	0.00604	0.0058
	Q_m	mg/g	5.952	9.174
	R^2	-	0.547	0.589
50	K_L	L/mg	0.00306	0.0082
	Q_m	mg/g	28.57	7.69
	R^2	-	0.558	0.605
60	K_L	L/mg	0.0051	0.0079
	Q_m	mg/g	20.83	15.625
	R^2	-	0.742	0.947
70	K_L	L/mg	0.0049	0.0063
	Q_m	mg/g	27.77	32.26
	R^2	-	0.771	0.838

Table 4. Data on Adsorption Isotherm Using the Freundlich Model

Temperature (°C)	Parameter	Controlled Bentonite	Cr(III) Doped Bentonite
30	K _F	0.000095	0.0051
	N	0.4283	0.592
	R ²	0.974	0.949
40	K _F	0.0046	0.0088
	N	0.857	0.6345
	R ²	0.907	0.945
50	K _F	0.0409	0.0038
	N	0.801	0.502
	R ²	0.988	0.970
60	K _F	0.029	0.018
	N	0.702	0.6035
	R ²	0.971	0.973
70	K _F	0.0049	0.062
	N	0.739	0.703
	R ²	0.962	0.991

Table 5. Gibbs Free Energy Data (ΔG), Entropy (ΔS), Enthalpy (ΔH), and Adsorption Capacity (Q_e) on Phenol Adsorption with Control Bentonite Adsorbent on the Influence of Temperature

Concentration (mg/L)	T (K)	Q _e (mg/g)	ΔS (kJ/Kmol)	ΔH (kJ/mol)	ΔG (kJ/mol)
25	303	0.2094	0.1962	70.669	11.21727
	313	1.0044			9.25512
	323	1.7862			7.29303
	333	2.3442			5.33099
	303	0.6420			10.62250
50	313	1.6746	0.1921	68.839	8.70129
	323	4.9956			6.77987
	333	5.4282			4.85856
	303	1.9398			8.23523
	313	6.9768			0.1149
323	7.2000	5.93736			
333	8.7210	4.78836			
303	3.2514	8.20184			
313	8.0094	0.1399	50.599	6.80259	
323	10.2282			5.40335	
333	16.7164			4.00410	
303	11.2602			6.28254	
313	14.0442			0.0558	23.196
323	15.9906	5.16613			
333	22.9812	4.60793			

Table 6. Gibbs Free Energy Data (ΔG), Entropy (ΔS), Enthalpy (ΔH), and Adsorption Capacity (Q_e) on Phenol Adsorption with Bentonite Adsorbs Doped with Cr(III) on the Effect of Temperature

Concentration (mg/L)	T (K)	Q_e (mg/g)	ΔS (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
25	303	0.9486	0.08002	32.674	8.42727
	313	1.1562			7.62705
	323	1.3116			6.82683
	333	2.9022			6.02661
50	303	3.9768	0.03895	18.041	6.23668
	313	4.1161			5.84708
	323	5.0375			5.45749
	333	6.7674			5.06789
75	303	5.7768	0.08104	30.722	6.16363
	313	7.3398			5.35319
	323	11.4844			4.54274
	333	13.1586			3.73229
100	303	7.0746	0.09761	35.426	5.85123
	313	7.2978			4.87516
	323	15.4746			3.89912
	333	17.6652			2.92304
150	303	19.4232	0.06897	25.815	4.91617
	313	19.6188			4.22644
	323	24.8371			3.53671
	333	37.0884			2.84698

From Tables 5 and 6, it is also seen that the adsorption capacity of Cr(III) doped bentonite has a higher value than the bentonite control. Entropy (ΔS) of phenol adsorption by control bentonite adsorbent and Cr(III) doped showed a degree of irregularity where a large tendency of entropy showed that the smaller the concentration and enthalpy (ΔH) there was a tendency to decrease with increasing concentration. It can also be seen that the Gibbs free energy data (ΔG) has a positive value because of a balanced state. This study according to previous research, Lyubchik [23] was report that the adsorption capacity also increases with increasing concentration.

Conclusion

Bentonite doped with metal oxide Cr(III) characterized by XRD shows that the diffraction angle shift (2θ) ie the diffraction angle (2θ) bentonite of 5.671 $^\circ$ shifts to the diffraction angle of 7.28 $^\circ$ which indicates the presence of another cation in the form of Cr(III) it is found between bentonite fields. The SEM results of the bentonite control had many gaps compared to Cr(III) doped bentonite, EDS results in the form of a decrease in Al, Si and Cr elements of 3.76%, 10.23% and 2.06%, respectively. The amount of adsorbate (phenol) absorbed at 80 minutes optimum time was 7.860% for control bentonite and 21.930% for Cr(III) doped bentonite. The kinetic model

used in bentonite control and bentonite doped by Cr(III) is pseudo-second-order. The isotherm model used is a Freundlich isotherm model that is multilayer adsorption. Enthalpy and entropy of the control bentonite and Cr(III) doped down with increasing phenol concentration and Gibbs free energy were positive because of the equilibrium condition.

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