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Adsorption Study on Phenol from Bentonite Doped with Zinc Oxide: Synthesis, Characterization, Equilibrium, Kinetics, and Thermodynamic

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Abstract

This study modified current bentonite with zinc oxide (ZnO) and investigated the performance of phenol adsorption. The material bentonite-ZnO was successfully synthesized and characterized with XRD, SEM-EDX, and FT-IR. The adsorption performance was determined by adsorption equilibrium, kinetics, and thermodynamic parameters. The adsorption, kinetic, and thermodynamic parameters were compared alternatively. The phenol adsorption capacity was obtained from Langmuir and Freundlich adsorption isotherm models, which for bentonite-ZnO was fit with both isotherm models (Langmuir R^2 = 0.997 and Freundlich R^2 = 0.9515) and was favourable than activated bentonite (n value bentonite-ZnO = 2.389; activated bentonite = 0.898). A kinetic model was tested with pseudo-first-order, pseudo-second-order, and intraparticle diffusion models which bentonite-ZnO and activated bentonite fit in the pseudo-second-order with an excellent agreement (R^2 = 0.999). Several thermodynamic parameters such as enthalpy, Gibbs free energy, and bentonite-ZnO have an entropy more than zero (ΔS = 0.008 J/mol.K), which demonstrated the feasibility and spontaneity ($\Delta G<0$) and endothermic nature (ΔH = 3.056 kJ/mol) of the phenol adsorption process. Several thermodynamic parameters such as enthalpy, Gibbs free energy, and bentonite-ZnO have an entropy more than zero (ΔS = 0.008 J/mol.K), which demonstrated the feasibility and spontaneity ($\Delta G < 0$) and endothermic nature (ΔH = 3.056 kJ/mol) of the phenol adsorption process. Based on the result data in this article, modified bentonite with ZnO has increased the ability for phenol adsorption than currently activated bentonite

Keywords: Adsorption kinetics, thermodynamics model, phenol, bentonite-ZnO

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Abstrak

Penelitian ini memodifikasi bentonit saat ini dengan seng oksida (ZnO) dan menyelidiki kinerja adsorpsi fenol. Material bentonit-ZnO berhasil disintesis dan dikarakterisasi dengan difraksi sinar-X (XRD), scanning electron microscopy-energy dispersive X-ray (SEM-EDX), dan Fourier transform inframerah (FT-IR). Kinerja adsorpsi ditentukan oleh parameter kesetimbangan adsorpsi, kinetika, dan termodinamika. Parameter adsorpsi, kinetik, dan termodinamika dibandingkan secara alternatif. Kapasitas adsorpsi fenol diperoleh dari model isoterm adsorpsi Langmuir dan Freundlich, dimana untuk bentonit-ZnO sesuai dengan kedua model isoterm tersebut (Langmuir R^2 = 0,997 dan Freundlich R^2 = 0,9515) dan lebih baik dibandingkan bentonit teraktivasi (nilai n bentonit-ZnO = 2,389; bentonit teraktivasi = 0,898). Model kinetik diuji dengan model difusi pseudo orde pertama, orde kedua semu, dan intrapartikel dimana bentonit-ZnO dan bentonit teraktivasi masuk dalam orde kedua semu dengan kesesuaian yang sangat baik (R^2 = 0,999). Beberapa parameter termodinamika seperti entalpi, energi bebas Gibbs, dan bentonit-ZnO mempunyai entropi lebih dari nol (ΔS = 0,008 J/molK), yang menunjukkan kelayakan dan spontanitas ($\Delta G < 0$) serta bersifat endotermik (ΔH = 3,056 kJ/ mol) dari proses adsorpsi fenol. Beberapa parameter termodinamika seperti entalpi, energi bebas Gibbs, dan bentonit-ZnO mempunyai entropi lebih dari nol (ΔS = 0,008 J/molK), yang menunjukkan kelayakan dan spontanitas ($\Delta G < 0$) serta bersifat endotermik (ΔH = 3,056 kJ/ mol) dari proses adsorpsi fenol. Berdasarkan data hasil artikel ini, bentonit yang dimodifikasi dengan ZnO mengalami peningkatan kemampuan adsorpsi fenol dibandingkan bentonit yang diaktivasi saat ini.

Kata Kunci:kinetika adsorpsi, model termodinamika, fenol, bentonit-ZnO

INTRODUCTION

Phenols and their derivatives are widely used in many petrochemical industries, petroleum refineries, and chemical or pharmaceutical industries which causes the level of waste containing phenol to be higher [1-3]. Phenolic compounds are an important problem because they cause severe hazards to human health and can inhibit or even eliminate microorganisms in the aquatic environment [4, 5]. Phenol itself exists as a crystalline substance that is colorless at room temperature and has hygroscopic properties in water and slightly in organic solvents that make them easily spilled or leaked into the surface water or inside groundwater sources [6]. Phenolic compounds have been enlisted as pollutants of priority concern by developed countries because the chemical compound is noted to be toxic and have severe short- and long-term effects on humans and other living organisms [7,8]. Phenol is classified as a hazardous material and harms health, either acute or chronic. The extended period of exposure to phenol can cause tremors, coma, and abnormal breathing when reaching human lethal doses estimated according to body weight [9]. Phenol derivatives with chlorine group are more toxic in aquatic environments, some of them that compound namely pentachlorophenol [10] and 2,4-dichlorophenol [11], which compounds classified as disruptor contaminant priority pollutant listed by the United States [12].

Phenol in aquatic environments is hazardous for all biotic organisms. The presence of phenols can reduce the biological biodegradation of other components. Therefore, phenol content in the effluent waste must be minimized at all costs. Various method can be used to reduce or even remove phenol compounds. Several processes have been used to remove these phenolic compounds Several methods is known for treating the phenol compound is distillation [13], adsorption [14,15], chemical oxidation [16], extraction, biodegradation with microorganisms like algae [17] or bacteria [18], with enzymatic [19,20] and electrochemical oxidation [21, 22]. Adsorption is the most effective method cause have several advantages for removing phenol from waste effluent or polluted water, such as low cost, easy operation, and high performance [23]. Activated carbons, kaolinite, bentonite, and montmorillonite is the most general adsorbent used to remove various pollutant in wastewater [25]. With the modification of the surface area of the adsorbent material, adsorption effectivity will increase, and the ability to remove organic compound was an increase [26]. The development of low-cost adsorbents like bentonite still being a hot research topic, as evidenced by the increasing number of publications every year [27].

Bentonite has adsorbing properties because its colloidal particle size is very small and has a high surface capacity. Activation of bentonite using acid will produce bentonite with a larger active site so that it will produce bentonite with a higher adsorption ability [28]. Modification of bentonite is needed, and potential exploring research which can increase the ability to adsorb organic harmful compounds [29]. Zinc (II) oxide (ZnO) is such an option to increase the surface absorptivity area of bentonite. ZnO is interesting due to its non-toxic nature, ability to absorb properties, chemical, mechanical, thermal stability, and synthesis feasibility [30, 31]. The use of zinc oxide nanoparticles, when compared to titania nanoparticles, has higher adsorption rates for heavy metals [32]. Zinc oxide has a weakness, such as instability of ZnO in acidic conditions, photo-corrosive nature, and spontaneous growth and aggregation restrict its applicability in wastewater treatment [33]. To overcome this problem, ZnO is usually applied by incorporating the material into porous materials such as bentonite. The symbiosis of these two materials can give the advantage to each other in adsorption study.

Research on the use of ZnO in adsorption studies is increasing. However, research on phenol adsorption on ZnO-doped Bentonite has not provided information about adsorption studies on the adsorption of phenol compounds. Research about bentonite-ZnO-modified material generally used to adsorb and degrade dyes compound [34-36]. The study of adsorption phenol and their mechanism using modified material was important to explain how the material adsorbs, chemical and physical properties change during and after adsorption, and improve the material's capabilities either by adding other materials or changing the material's structure [37].

In this research, bentonite doped with ZnO applied on phenol adsorption, which includes adsorption equilibrium, kinetics, and thermodynamics and its relationship with the effect of concentration and temperature on the adsorption study. The bentonite doped with ZnO compounds will be characterized and used for the application of the adsorption of phenol. Modified bentonite was compared with nonmodified bentonite, and. The results of the studies will determine which material has been optimal as expected to be able to become an adsorbent to adsorb phenol. The adsorption parameters tested included kinetic adsorption parameters (pseudo-first-order, pseudo-second-order, intraparticle diffusion), adsorption isotherm (isotherm Langmuir and Freundlich), and thermodynamics (enthalpy, entropy, and Gibbs free energy) to compare effectivity bentonite-ZnO against activated bentonite.

MATERIALS AND METHODS

Materials

The materials used in this study consisted of natural bentonite from PT. Indonesian Natural Bentonite, aquadest (H_2O), sulfuric acid (H_2SO_4) Merck, phenol (C_6H_5OH) Merck, hydrochloric acid (HCl) Merck, sodium hydroxide (NaOH) Merck, sodium carbonate (Na_2CO_3) Merck, reagent follinciocalteu Merck and zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$) Merck.

Bentonite preparation and activation

The preparation and activation of bentonite, according to Kumararaja et al. [38], is 50 grams of natural bentonite added to 500 mL of distilled water in a 1000 mL beaker and then stirred using a stirrer for 24 hours. After that, the mixture is acidified with 250 mL H_2SO_4 2M and stirred using a stirrer again for 10 hours. The suspension formed is allowed to settle until it settles, then the supernatant is removed, and the remaining sediment is added with distilled water. This is done continuously until the pH is around 5. The precipitate obtained is then separated using centrifugation at a speed of 4000 rpm for 10 minutes at room temperature. The precipitate obtained was dried using an oven at 100 °C until dry and sieved with a 200-mesh sieve

ZnO doping solution preparation and bentonite modification by doping process using ZnO

Preparation of the ZnO doping solution, according to Pajarito et al. [39], is as much as 7.18 g of zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) dissolved with distilled water up to 50 mL in a measuring flask and obtaining a $ZnSO_4$ 0.5 M solution. This $ZnSO_4$ solution was then dripped slowly into 50 mL NaOH 0,5 M solution for 30 minutes. Furthermore, the mixed solution was stirred using a stirrer at room temperature at a constant speed for 2 hours, and a doping solution was obtained ZnO.

Furthermore, the doping process of ZnO into bentonite was carried out according to Parimaladevi & Suganya [40] with modifications. A total of 12 g of activated bentonite was dissolved by adding 120 mL of distilled water. After that, the white ZnO doping solution is dropped gradually into the bentonite until the white solution runs out. Then stirred using a stirrer for 24 hours at room temperature. The mixture that has been stirred using a stirrer is separated utilizing centrifugation at a speed of 4000 rpm for 10 minutes. The precipitate obtained was then dried using an oven at a temperature of 200 °C for 24 hours. The solid was ground until smooth, then sieved using a 200-mesh sieve and stored for characterization using XRD, FTIR, and SEM-EDX.

Adsorption studies of Phenol

Adsorption phenol was carried out with some parameters, including time, concentration, and temperature parameters according to Ai et al. [41] and Elmoubarki *et al.* [42], with modification. Activated bentonite and bentonite-ZnO 0.05 g exactly were added to 30 mL of phenol with various concentrations. The mixture is stirred with a horizontal shaker at various times of adsorption and various temperature. The phenol, which has been through the adsorption process, is separated using centrifugation, the filtrate obtained is diluted 10 times, and 5 mL is taken. Then 0.5 mL of follinciocalteu reagent was added and incubated for 5 minutes at room temperature. This mixture is then added to 1 mL Na_2CO_3 5% and incubated again for 1 hour. The absorbance of each will be measured using a UV-Vis spectrophotometer at λ max = 765 nm. Parameter of studies using various concentrations (25, 50, 75, and 100 mg/L) for determined isotherm model adsorption, various temperatures (30, 40, and 60 °C) for determined enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), when various time (0, 20, 30, 40, 50, 60 minutes) for determined adsorption kinetic model.

Adsorption of phenol against activated bentonite and ZnO-bentonite by FT-IR Spectrophotometer

The doping process was studied spectroscopically to see the changes that occurred in the adsorbent before and after the adsorption process was carried out. A total of 0.05 g of control bentonite and ZnO-bentonite were added with 30 mL of phenol. The mixture was then stirred using a horizontal shaker for 30 minutes and filtered. The solid obtained is dried at 100 °C. Furthermore, the solid is characterized using a Fourier transform infrared (FTIR) spectrophotometer to indicate a change before or after adsorption.

Data analysis

Data of phenol adsorption obtained from spectrophotometer UV-Vis (absorbance) collected and calculated for percentage of Removal (%) and adsorption capacity (Qe) value with the equation:

$$\text{percentage of Removal } (\%) = \left(\frac{C_0 - C_t}{C_0}\right) x\ 100\% \qquad (1)$$

$$\text{Adsorption Capasity } (Qe) = \frac{(C_0 - C_t) x\, V_{solution}}{m_{adsorbent}} \qquad (2)$$

Note
C_0 = concentration before adsorption,
C_t = concentration after adsorption,
V solution = solution volume,
M adsorbent = mass of adsorbent

RESULTS AND DISCUSSION

Characterization of bentonite-ZnO

Bentonite is a layered clay that contains a lot of montmorillonites; before bentonite is applied, it needs to be activated first. The activation process is carried out by adding an acid such as sulphury acid (H_2SO_4). This aims to make bentonite have a greater surface acidity, good porosity and remove impurities so that the bentonite surface is more open which allows cation exchange to occur more frequently [43, 45]. The cations in bentonite will be exchanged with ZnO metal oxide so that the doping process occurs. As explained by Keeling et al. [46], montmorillonite has a cation-exchange capacity and expands. The difference between inactivated bentonite, activated bentonite, and Bentonite-ZnO lies in the color of the powder; inactivated bentonite still contains impurities so that it looks blackish gray; activated bentonite has a gray color. As a result, activation process, Bentonite-ZnO has a grayish-white color cause the ZnO compound is doped in a layer of bentonite. The difference between the three can be seen in **Figure** 1.

(a) (b) (c)

Figure 1. Solid form of (a) bentonite-ZnO, (b) bentonite without activation, (c) activated bentonite

Activated bentonite and Bentonite-ZnO were characterized using XRD, which aims to see the shift in the diffraction angle (2θ) between the two. The results of XRD characterization can be seen in **Figure** 2.

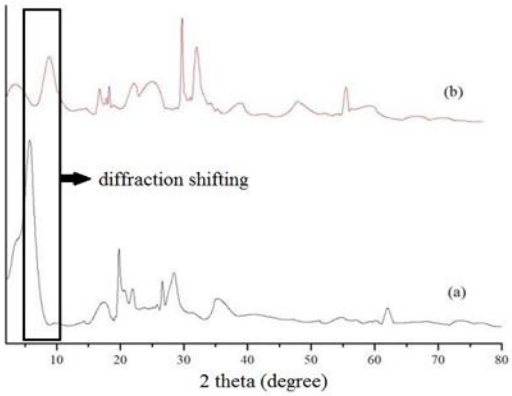


Figure 2. XRD spectrum: (a) activated bentonite and (b) Bentonite-ZnO

The appearance of the diffraction angle (2θ) at 32.361° and 34.89° is a characteristic of ZnO [46], and the shift of the angle for montmorillonite minerals to

6.64° and 19.73° indicates that the doping process has been successful. According to Oueslati et al. [47], the diffraction angles for montmorillonite are at 5.671° and 19.738°. If bentonite is doped by a compound, there will be a shift in the diffraction angle in the 3-10° area, which is characteristic of bentonite [48]. XRD digital data for Be-ZnO shows the amount of d-spacing in accordance with JCPDS data No. 89-0510. According to Seftel et al. [49], another peak that appears on the diffractogram shows that the solid obtained is a mixture and amorphous material.

Characterization using SEM-EDX aims to see the success of doping on the bentonite surface with ZnO metal oxide [50]. SEM results can be seen in Figures 3 when in **Figures** 3 (a) and 3 (b), activated bentonite still has many gaps, while in **Figures** 3 (c) and 3 (d), the gaps are beginning to close and appear tighter surfaces. This indicates that the bandgap on the bentonite surface has been filled by ZnO.

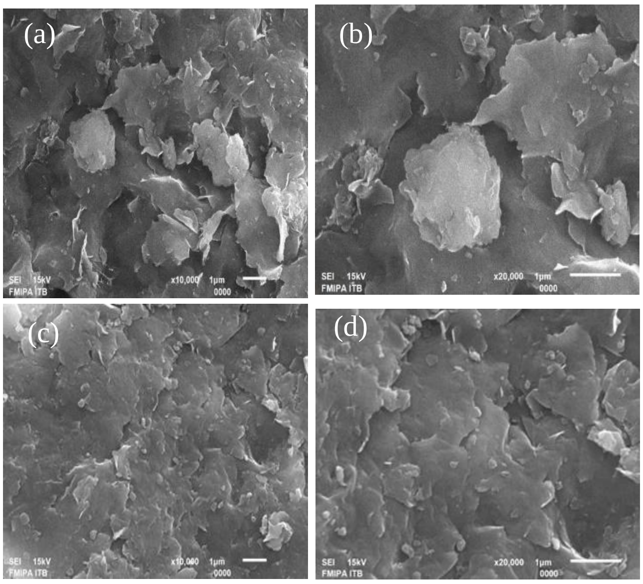


Figure 3. SEM of (a) activated bentonite zoom in 10.000x, (b) activated bentonite zoom in 20.000x, (c) Bentonite-ZnO zoom in 10.000x, (d) Bentonite-ZnO zoom in 20.000x.

The results of EDX can be seen in **Table** 1, where there is a decrease in the percentage of elements in activated bentonite, especially Al and Si located in montmorillonite. The doping process with ZnO will increase the percentage of Zn metal oxide. Table 1 shows a decrease in the percentage of Al elements from 7.53 to 6.96%. While the Si element was originally 19.84 to 18.21%, there is a Zn content of 1.92% and Na of 3.53%. The content of the element Na which is more than Zn, does not affect the absorption of phenol because phenol will be more easily attracted by Zn because of its larger molecular size and its more reactive nature. The doping process with ZnO will increase the percentage of the Zn metal oxide. So, it can be concluded that the ZnO doping process into bentonite has been successfully carried out.

Table 1. Analysis of elements using EDX

Adsorbent	Al (%)	Si (%)	Na (%)	Zn (%)
Activated bentonite	7.53	19.84	-	-
Bentonite-ZnO	6.96	18.21	3.53	1.92

The addition of ZnO metal oxides allows the doping ZnO compound to attach to the surface of bentonite, and van Der Waals bonding occurs. According to Xu et al. [51], ZnO particles will stick and spread on the surface of bentonite. Bentonite blocks the buildup of fellow ZnO particles causing the surface area of ZnO particles to get larger, resulting in a greater ability for bentonite to adapt. Phenols are one of the compounds that have hydroxyl groups and are considered as one of the adsorption sites. Adsorption can occur through interactions between electrons π from aromatic rings. ZnO metal oxide will cause electrons π phenols to be pulled due to the oxidation process. So that the presence of oxide ZnO metal will enlarge bentonite's ability to adapt to phenol [27].

Characterization using FTIR aims to find out the existence of function clusters in activated bentonite and Bentonite-ZnO. After these two adsorbents absorbs phenols, it is also done characterization using FTIR to see the shift in wavenumbers caused by the function group -OH in phenols.

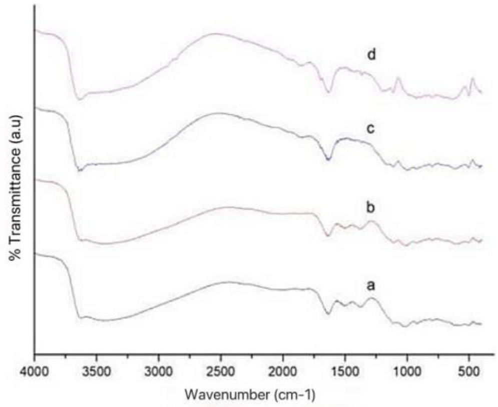


Figure 4. FTIR spectrum of (a) activated bentonite and (b) after absorbing phenol, while (c) Bentonite-ZnO and (d) after absorbing phenol

FTIR Activated bentonite spectrum can be seen in **Figure** 4(a), which indicates the presence of absorption band at wavenumber 3363.86 cm^{-1}, indicating H-OH vibration, while the wavenumber is 1633.71 cm^{-1} is the bending vibration of H-OH. There is a vibration of Al-O-Al stall at 1010.71 cm^{-1} and there is a bending vibration of Si-O-Si at wave number 920.05 cm^{-1} [52, 53]. The activated bentonite spectrum that already absorbs phenols in **Figure** 4(b) has the same absorption tape as **Figure** 4(a). It is stated that the wavenumber of Zn-O metal oxide absorption is found at 501.49 cm^{-1} as shown in **Figure** 4(c) [54]. The difference between **Figure** 4(a) and 4(b) is that the intensity of the wave number is increasing. Wavenumber 3211.48 cm^{-1} indicates H-OH tendril vibration while at wavenumber 1614.42 cm^{-1} is H-OH bend vibration. At wavenumber 921.97 cm^{-1} there is a vibration of bending Al-O-Al and at the wave number 1633.71 cm^{-1} is the vibration of bending Si-O-Si. The Bentonite-ZnO spectrum that has absorbed phenol in Figure 4(d) has the same absorption tape as **Figure** 4(c). Adsorbent Be-K and Be-ZnO that have absorbed phenols do not show significant peaks for -C=C- of phenols. Vibration –C=C– usually appears on wavenumbers 1450-1600 cm^{-1}. This is because the comparison of absorbed phenols is much smaller compared to bentonite, so the typical peak of phenol is covered by bentonite vibrations whose peaks are widened. Based on that data, FTIR is not proven phenol absorbed by bentonite, but will be taken measurements with UV-vis spectrophotometer to see the adsorption process.

Effect of concentrations and equilibrium model adsorption

The variation in the initial phenol concentration was investigated by using different concentrations of phenol in the range 20-100 mg/L with an adsorbent dose 1.6 g/L, time 20 minutes and temperature 30^{0}C. **Figure** 5. show the % removal phenol on Bentonite-ZnO decreased slowly at 20-80 mg/L and dropped significantly in 100 mg/L when activated bentonite do the same and increase slowly. According to Abdelkreem [55] higher concentrations cause more power to make the liquid phase enter the dense phase, in this case phenols and bentonite. So that the adsorption will decrease as the concentration increases. That data explains that the site of Bentonite-ZnO even though activated bentonite still has a good site adsorption at have large surface area. Removal phenol at a concentration 20 mg/L in Bentonite-ZnO has a higher value than activated bentonite which it shows that modified adsorbent has the greatest ability to adsorb phenol in solution. ZnO compounds as nanograins on the surface widen the pores of bentonite causes enlarge the active site of the adsorbent to absorb the adsorbate [56].

Adsorption isotherm model is represented as the number of adsorbate molecules per unit mass of adsorbent as a function of equilibrium concentration in bulk solution at a constant temperature [57]. Adsorption isotherms are useful for understanding the mechanism of the adsorption. Langmuir and Freundlich isotherm models were chosen in this study for evaluating the relationship between the amount of phenol adsorbed by bentonite-ZnO compared with activated bentonite and its equilibrium concentration in aqueous solution [58].

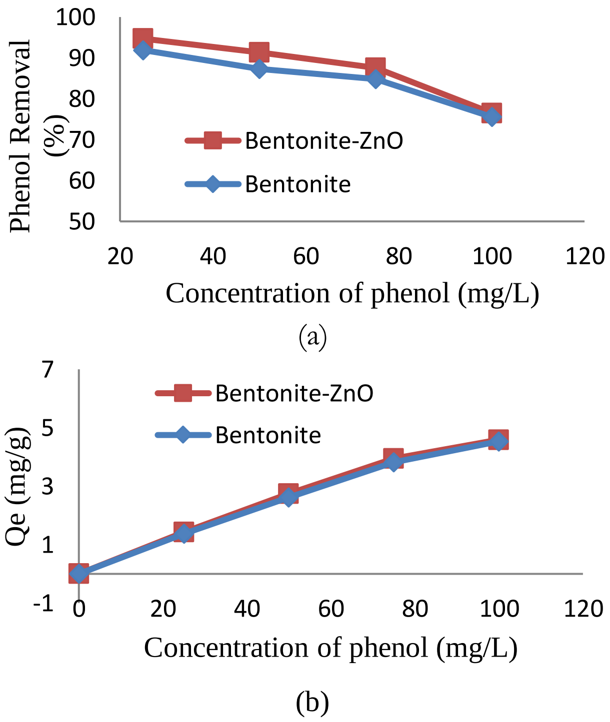


Figure 5. The percentage of (a) phenol removal and (b) adsorption capacity

Adsorption isotherm model is represented as the number of adsorbate molecules per unit mass of adsorbent as a function of equilibrium concentration in bulk solution at a constant temperature [57]. Langmuir and Freundlich isotherm models were chosen in this study for evaluating the relationship between the amount of phenol adsorbed by bentonite-ZnO compared with activated bentonite and its equilibrium concentration in aqueous solution [58].

The Langmuir model assumes that adsorption takes place at specific homogeneous sites on the surface of the adsorbent and also, when a site is occupied by an adsorbate molecule, monolayer adsorption, and the energy of the adsorption is constant. Langmuir isotherm model can be presented in linear equation by as Eq. 3:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m} C_e + \frac{1}{Q_m} \qquad (3)$$

where C_e is the equilibrium concentration of the adsorbate ions (mg/L); q_e is the amount adsorbed (mg/g); and Q_m and K_L are Langmuir constants correlated to the maximum monolayer adsorption capacity (monolayer capacity) (mg/g) and energy of adsorption (L/mg), respectively. The maximum adsorption capacity (Q_m) is calculated by plotting the curve 1/qe vs 1/Ce which gives the maximum adsorption capacity as well as the Langmuir constant which relates to the energy of adsorption. The essential features of the Langmuir isotherm model can be expressed in terms of "R_L" a dimensionless constant, separation factor or equilibrium parameter [59] with equation represented by Eq. 4:

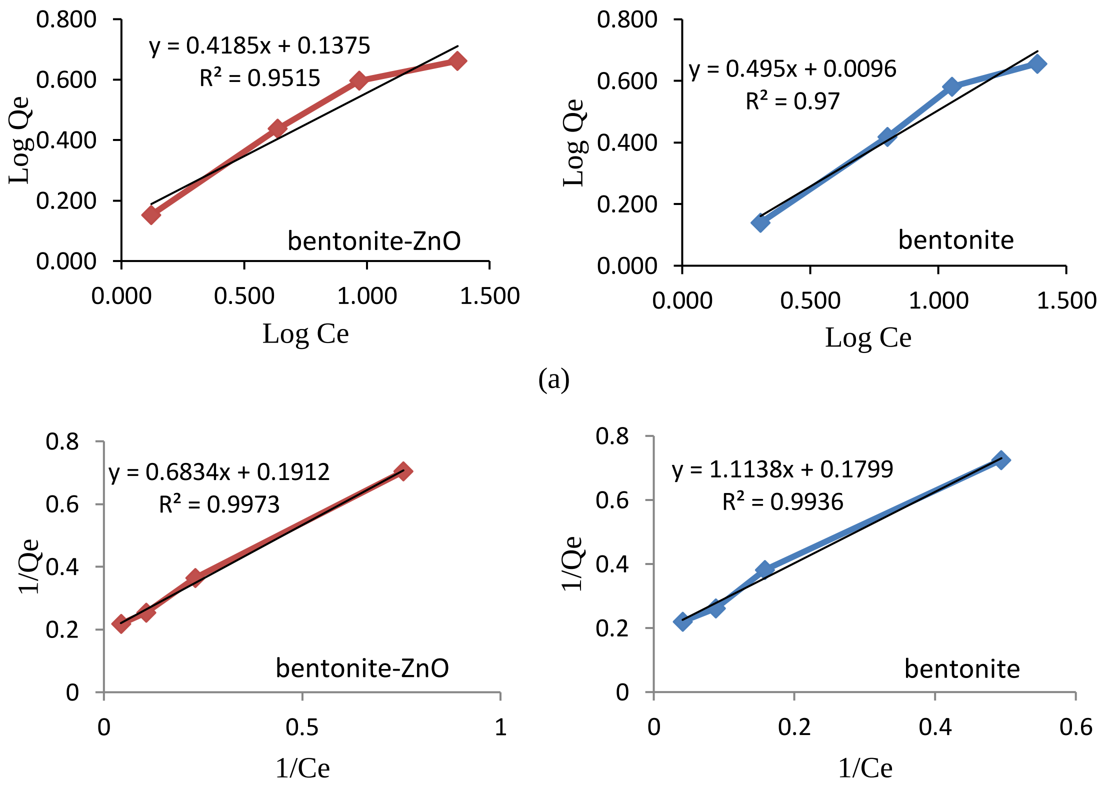
$$R_L = \frac{1}{(1+C_0 K_L)} \qquad (4)$$

where *Co* (mg/L) is the initial amount of adsorbate and *b* (L/mg) is the Langmuir constant described above. The R_L parameter is considered as more reliable indicator of the adsorption. There are four possibilities for the R_L value which is $0<R_L<1$ (favorable adsorption), $R_L>1$ (unfavorable adsorption), $R_L=1$ (linear adsorption), and $R_L=0$ (irreversible adsorption).

Isotherm Langmuir for activated bentonite and bentonite-ZnO was presented by **Table** 2 and **Figure** 6. The result shows that both adsorbents fit isotherm Langmuir. This is evidenced by the correlation coefficient value of approximately 1 which linearity graph (R^2 value) for activated bentonite and bentonite-ZnO are 0.993 and 0.997, respectively.

Table 2. Isotherm Models for adsorption phenol solution using adsorbents.

Materials	Isotherm Langmuir				Isotherm Freundlich			
	R^2	Q_m	K_L	R_L	R^2	K_F	n	1/n
bentonite-ZnO	0.997	5.23	0.2798	0.0345	0.95	1.372	2.389	0.4185
bentonite	0.993	5.56	0.1615	0.0583	0.97	1.513	0.898	1.1138



(a)

(b)

Figure 6. (a) Isotherm Freundlich model and (b) Langmuir model graph

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The RL value for the adsorption of phenol on to two adsorbents is observed to be in the range 0 to 1; this range investigates the favorable adsorption method. These results can be explained, as the hypothesis of the Langmuir isotherm equation is based upon the monolayer coverage of adsorbate molecule over a homogeneous surface of the adsorbent material, which means that the material surface consists of similar active sites [60].

Effect of time and kinetics model adsorption

The variation in time adsorption phenol was investigated by using different concentration of phenol 100 mg/L with adsorbent dose 1.6 g/L, time in range 20-60 min and temperature 30 °C.

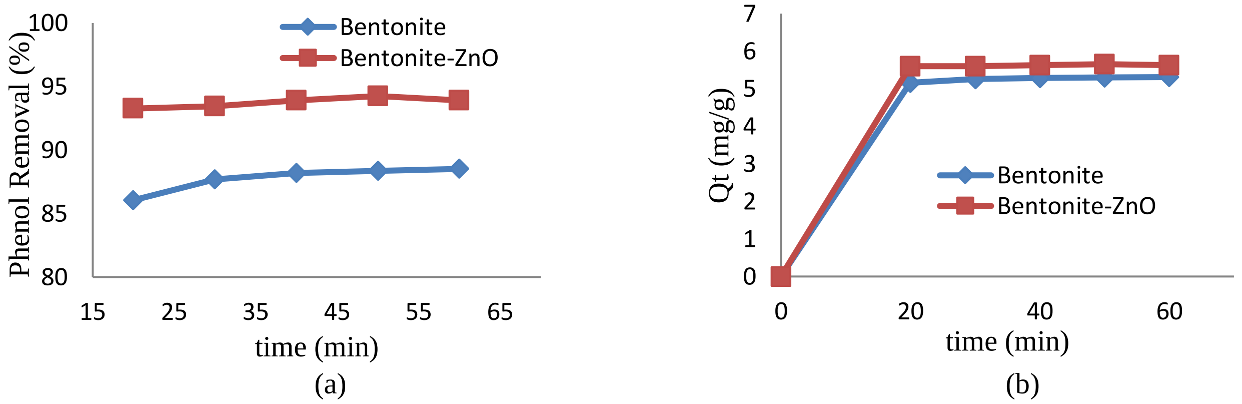

Figure 7. effect of time on removal phenol and adsorption capacity

Figure 7 show the percentage removal phenol on Bentonite-ZnO increase rapidly at 20 min and stagnant until over time while in activated bentonite do the same. The adsorption capacity (Qt) of phenol increased with the increase of time and finally reached the saturation [62]. The saturation state of adsorption phenol was in 20 min by bentonite-ZnO (93.26%) while in activated bentonite was in 30 min (87.69%). At start 20-min, bentonite-ZnO and activated bentonite have a significant absorptivity on phenol solution with percentage removal value are 93.26 and 86.05%, respectively. This result can conclude that modified adsorbent has better ability than normal adsorbent.

The adsorption kinetics is one the most important data in order to understand the mechanism of the adsorption and to assess the performance of the adsorbents. Different kinetic models including the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied to predict the adsorption kinetics for modified adsorbent and its compared. The best-fit of the kinetics model is designated based on the linear correlation coefficient values. Lagergren's first-order kinetic equation is used to describe the solute adsorption on various adsorbents based on adsorbent capacity [63]. This kinetics model describes the adsorption rate and depends on the available sites in the adsorbent for physisorption process. The Lagergren first-order equation is expressed as Eq. 6:

$$Ln\,(Q_e - Q_t) = LnQ_e - K_1 t \qquad (6)$$

where, Qe and Qt are the amounts of phenol ions sorbed (mg/g) at equilibrium and at time (min), respectively; and K_1 (min) is the first-order reaction rate constant. The calculated values of K_1, Qe from the equation and the correlation coefficient (R^2) value for fitting the first-order rate model. A straight line of ln (Qe −Qt) versus *t* suggests the applicability of this kinetic model, and Qe and K_1 can be determined from the intercept and slope of the plot, respectively. Pseudo-second-order by Ho [23] describes the adsorption reaction rate with dependent energetically heterogeneous sites on the adsorbent; it is considered a chemisorption model [64]. The pseudo-second-order equation is expressed as Eq. 7:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad (7)$$

where K_2 (g/mg.min) is the rate constant of the second-order equation. The plot of t/Qt versus t should give a straight line if pseudo-second-order kinetic model is applicable and Qt and K_2 can be determined from slope and intercept of the plot, respectively. Inter-particle diffusion model investigates the inter-particle uptake of adsorbate and the pore diffusion in adsorption. This gives an indication of the thickness of the boundary layer. The intraparticle diffusion model equation is expressed as Eq. 8:

$$Q_t = K_{id}t^{1/2} + c \qquad (8)$$

where K_{id} (mg/g$\sqrt{t}$) is the rate constant of intraparticle diffusion model. The values of K_{id} and c can be determined from the slope and intercept of the straight line of Qt versus $t^{1/2}$, respectively.

The data kinetic model's experimental data on bentonite-ZnO and activated bentonite represented by **Table** 3 and **Figure** 8.

Table 3. Kinetic Models for adsorption phenol solution using adsorbents

Adsorbent	Qe (exp)	Pseudo-first-order			Pseudo-second-order			Intraparticle Diffusion		
		$Qe_{(cal)}$	K_1	R^2	$Qe_{(cal)}$	K_2	R^2	K_{id}	c	R^2
Bentonite-ZnO	5.655	0.535	0.008	0.807	7.072	0.106	0.999	0.0161	5.525	0.743
Activated-Bentonite	5.655	0.272	0.08	0.262	5.668	0.649	0.999	0.0425	5.001	0.839

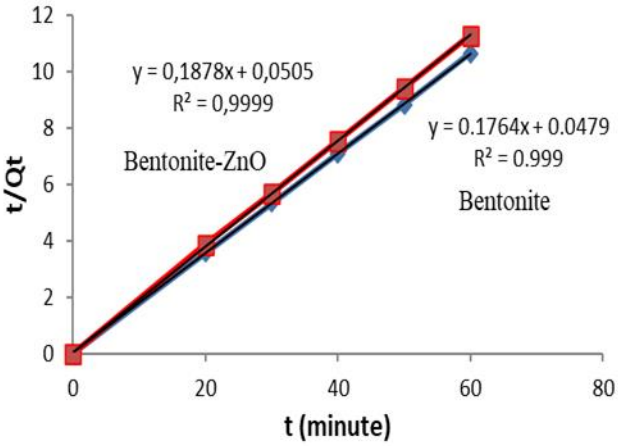

Figure 8. Pseudo-second-order graph in adsorption phenol using adsorbents

The result of experiment data shows the modified adsorbent and its compared were not suitable with pseudo-first-order because the correlation coefficient value is too low which may be indicative of a bad correlation. In **Figure** 8, pseudo-second-order of all adsorbent is fit with correlation close to unity (R^2 =0.9999). The correlation coefficient (R^2) of pseudo-first-order and pseudo-second-order kinetic models were in the range of 0.88−0.93 and 0.99, respectively [65]. The intraparticle diffusion model was not suitable for this adsorption studies cause the correlation is too low even the c value is high than unity which the adsorbent has a larger boundary effect [57]. From the experimental result of kinetic model, the pseudo-second-order was found to be the best fitted on bentonite-ZnO and activated bentonite which mean the process of phenol adsorption considered as a chemisorption model

Effect of temperature and thermodynamic adsorption

The variation in time adsorption phenol was investigated by using different concentration of phenol 100 mg/L with adsorbent dose 1.6 g/L, time in 20 min and temperature at 30, 40, and 60^{0}C. Figure 9 show the bentonite-ZnO have a consistently increase for ability phenol adsorption with a small amount when activated bentonite increased gradually with increasing temperature in these studies.

This behavior from modified adsorbent may be owing by chemical interaction between phenol and ZnO material which were attached in bentonite. This reason is also strengthened by Elkady et al. [60] which said that the rate of intraparticle diffusion of phenols into the pores of the magnetic adsorbent is enhanced, and that may create new reaction sites on to the magnetic ZnO at high solution temperature. bentonite-ZnO and activated bentonite on 20^{0}C have a different activity of phenol removal with % removal phenol value is 93.42% and 87.36%, respectively.

This conclude that modified bentonite was have better ability than their compared.

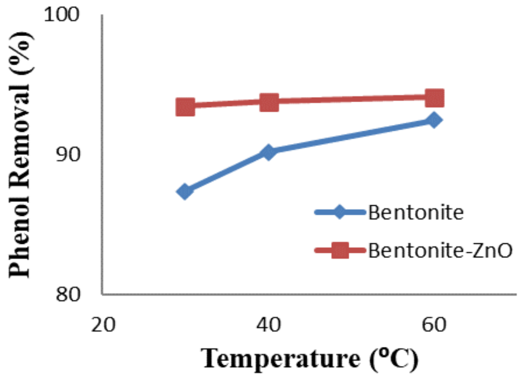

Figure 9. Effect of temperature on removal phenol by modified adsorbent and their compared.

Thermodynamic parameters are very important for studies of any adsorption to check the spontaneity and feasibility of the adsorption process. They provide necessary information to design an adsorption process. Thermodynamic parameters usually check for experimental data such as heat of enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) which govern the feasibility and spontaneity of adsorption process. The thermodynamic study was calculated by Eq. 8-9:

$$Ln\ K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (8)$$

$$\Delta G = \Delta H - T\ \Delta S \qquad (9)$$

where ΔG (kJ/mol) is Gibbs free energy, K_d is coefficient distribution of solute can be obtained by Qe/Ce, ΔH (kJ/mol) is enthalpy of adsorption, and ΔS (kJ/mol) entropy of adsorption which can be calculated using the plot of ln K_d vs −1/T to have a linear equation.

Table 4 represented the result of calculated thermodynamic adsorption for modified and compared adsorbents on phenol adsorption.

Table 4. Thermodynamic parameters for adsorption phenol solution using adsorbents

Adsorbent	Temperature (K)	ΔS (J/molK)	ΔH (kJ/mol)	ΔG (kJ/mol)	R^2
Bentonite-ZnO	303	0.008815	3.05606012	-5.7224	0.977
	313			-5.8104	
	333			-5.9864	
Bentonite	303	0.044285	15.5529998	2.1603	0.9758
	313			1.7183	
	333			0.8343	

The calculated value of bentonite-ZnO gives a negative charge Gibbs free energy value whose value always decreases with increasing temperature. That data allowing predictions about the spontaneous and thermodynamically favorable nature of the phenol designates that the adsorption process is endothermic in nature. The positive value of entropy change (ΔS) for all adsorbents is shows an increase in disorder at the solid/liquid interface through the phenol sorption process [66]. From the thermodynamic data result, it is concluded that bentonite-ZnO have a better ability on standard temperature range for adsorption phenol than activated bentonite because ZnO compound which attach in that adsorbent. adsorption process on to modified bentonite. That reason is compatible with research on ZnO material that it increases the driving force of adsorption process. The positive value of ΔH for all adsorbents.

CONCLUSION

Bentonite modified with ZnO compound was successfully synthesized and will used as an adsorbent for removal phenol. The bentonite-ZnO has better ability against activated bentonite. Improvement in activated bentonite using ZnO for adsorption phenol solution has a positive impact on the percentage of phenol decontamination. The mathematical modeling suggested that phenol decontamination using bentonite-ZnO includes both chemical and physical adsorption processes (Langmuir R^2 = 0.997 and Freundlich R^2 = 0.9515). On the other hand, it was evident that the adsorption of phenol on to bentonite-ZnO was described well by the pseudo-second-order reaction rate model with excellent agreement (R^2 = 0.999), which allows a prediction that the studied sorption system is controlled by a chemisorption process. Finally, Estimation of the thermodynamic parameters (ΔH, ΔG, and ΔS) demonstrates the spontaneous and endothermic nature of the phenol sorption process. However, a positive value of ΔS indicates increasing randomness at the solid/liquid interface during the adsorption of phenol on to bentonite-ZnO.

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