

*Full Length Research Paper*

## Adsorption of phenol on natural clay

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Natural clay being locally abundant and cheap material in Algérie can be easily activated to become a promising adsorbent for phenol removal from aqueous solution. The natural clay before and after activation was characterized using XRD and IR techniques. The effects of various experimental parameters, such as initial phenol concentration, temperature, pH, contact time and adsorbent dose on the adsorption extent were investigated. Langmuir adsorption model was used for the mathematical description of the adsorption equilibrium and the equilibrium data fitted very well with this model. The activated natural clay had the monolayer adsorption capacity equal to 15 mg/g at pH value of 5.0 and 23°C, adsorption measurements show that the process is very fast and physical in natural clay. The extent of the phenol removal increased with the decrease in the initial concentration of the phenol and contact time of solution. The results showed that as the amount of the adsorbent was increased, the percentage (%) of phenol removal increased accordingly. Thermodynamic parameters showed that the adsorption of phenol on activated natural clay was exothermic.

**Key words:** Phenol, activated clay, adsorption isotherm, thermodynamic parameters, montmorillonites, adsorbent, x-ray diffraction.

### INTRODUCTION

Organic contaminants from industrial waste that seriously threaten the human health and the environment, has been recognized as an issue of growing importance in recent years. Phenolic compounds are commonly produced in wastewater generated by petrochemical, oil refineries, coal conversion, steel plant, paint and phenol-producing industries (Aygiin et al., 2003), phenols are the most common in water, considered highly toxic (APHA, AWWA and WEF, 2006) even at low concentrations. Their high toxicity and difficulties in their biodegradation, generally closely related to functional group presence (e.g. chlorophenols), seriously threaten the human health and the environment, leading to the establishment of rigid limits on the acceptable environmental levels of phenol. They are found in effluents generated by various different industrial activities as well as associated with agricultural activities, especially due to the excessive use of

chlorinated pesticides.

Adsorption process is a prominent method for removal of organic pollutants practically used by industries. Accordingly, abundantly reported findings were carried out on adsorption process using activated carbon. However, superior activated carbon is expensive and efforts to utilize low-cost adsorbent become a great intention. Thus, the aim of this study was to explore the potential of modified montmorillonite adsorbent for adsorption of phenol and other pollution parameters, and some heavy metals. The performance of activated montmorillonite was compared with the natural montmorillonite. There are some literature references concerning the phenol adsorption on organobentonite (Juang et al., 2002; Vianna et al., 2004; Hall et al., 1996), but in our opinion they need further verification, especially in respect to the pH and its influence on the phenol uptake by adsorbent.

The prime objectives of the present investigation were to conduct the batch sorption tests, which included determination of sorption kinetics and isothermal

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adsorption capacity of the sorbent and to assess the effect of pH on the removal of phenol from synthetic waste water.

## MATERIALS AND METHODS

The clay used in this study was Algerian montmorillonite from Rousselin Mghnia (West Algeria). This Algerian montmorillonite clay was supplied by Chemical Ltd., Algerian Research Company of Non Ferreux (ENOF), Algeria. For this clay material, the cation exchange capacity (CEC) = 90 meq/100 g was assumed.

The natural clays were washed several times with distilled and deionised water and were completely dispersed in water. After 17 h at rest, the dispersion was centrifuged for one hour at 2400 rpm. The size of the clay particles obtained was < 2  $\mu\text{m}$ .

These clay particles were dispersed in water and heated at 75°C in the presence of a solution composed of the sodium salts of bicarbonate (1 M), citrate (0.3 M), and chloride (2 M). The purpose of this operation was to eliminate inorganic and organic compounds, aluminium found in the inter-layer spaces and various free cations. Carbonates were removed by treatment with HCl (0.5 M) and chloride was eliminated after several washings. The organic matter was eliminated completely by treatment with  $\text{H}_2\text{O}_2$  (30% v/v) at 70°C. The purified clay was dried at 110°C, then saturated with sodium ( $\text{Na}^+$ ). To ensure complete transformation into the sodium form, all samples were washed several times with a NaOH solution (1 M). Purity of the natural clay samples before and after activation was tested by IR spectral analysis. An IR transmittance spectrum of the ground samples was obtained in the 4000 to 400  $\text{cm}^{-1}$  range on Perkin-Elmer FT 1720 spectrometer.

Purity of the natural clay samples before and after activation was also determined by the analysis of the X-ray diffraction (XRD) spectra, which involved the identification and semiquantification of the characteristic peaks of the minerals present. A Philips diffractometer with D5000 Ni-filtered  $\text{CuK}\alpha$  radiation used was 1, 5406 Å. natural clay samples before and after activation with both randomly and preferred orientation were scanned over the interval 5 to 80°2 $\theta$  at scanning speeds of 0.03°/5 s.

## RESULTS AND DISCUSSION

### Natural clay characterization

Results of the X-ray diffraction analysis for activated and activated clay are shown in Figure 1. Figure 1 clearly shows that the d spacing of clay increased from 10.27 to 12.11 Å, which could be attributed to the activated clay. Quartz (reflection at  $d = 2.89$  Å,  $2\theta = 35.97^\circ$ ) and calcite (reflection at  $d = 2.89$  Å,  $2\theta = 35.97^\circ$ ) are the major impurities. The purified sample with Na-exchange shows the position of the 001 (reflection at 12.11 Å,  $2\theta = 5.37^\circ$ ) characteristic of sodium and Kaolinite (reflection at  $d = 5.41$  Å,  $2\theta = 19.03^\circ$ ).

Figures 2 and 3 present the spectra IR of natural and activated clay. The examination of these spectra revealed following characteristic absorption bands: The IR spectra of the clay samples were recorded over the spectral range 400 to 4000  $\text{cm}^{-1}$ . In fact, IR techniques had been used by many researchers for identification of natural

clay minerals (Hajjaji et al., 2001). The obtained characteristic bands of kaolinite appeared at 3618.67, 3641.59, 1100.39, 907.602, 830.38, 758.355, 521.24 and 456.84  $\text{cm}^{-1}$  (Gadsden, 1975). The high intensity of the peak appearing at 1100.78  $\text{cm}^{-1}$  was an indication of the large amount of this mineral in the sample. The band at 1100.78  $\text{cm}^{-1}$  was attributed to Si-O stretching. The bands at 830.38 and 521.24, 456.84  $\text{cm}^{-1}$  were assigned to Si-O-Al and Si-O-Mg, Si-O-Fe and bending vibrations respectively (Gadsden, 1975; Madejova, 2003). This indicated that most part of the layer charge resulted from trivalent ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) to bivalent ( $\text{Mg}^{2+}$ ) ion substitution in the octahedral sheet. These functional groups were present in silicate minerals such as kaolinite and montmorillonite. The band observed at 3412.41  $\text{cm}^{-1}$  is assigned to stretching vibrations of adsorbed water molecules. Another characteristic band for bending vibrations of adsorbed water usually appeared at 1650 to 1600  $\text{cm}^{-1}$  as a medium band (Gadsden, 1975). The stretching vibrations of the surface hydroxyl groups (Si-Si-OH, or Al-Al-OH) were found at 3618.67 and 3641.59  $\text{cm}^{-1}$ . The characteristic bands of montmorillonite-Na were observed at 1036.39 and 456.20  $\text{cm}^{-1}$  (Gadsden, 1975). The high intensity of the peak appearing at 1036.39  $\text{cm}^{-1}$  was an indication of the large amount of this mineral in the sample. The band at 1036.39  $\text{cm}^{-1}$  was attributed to Si-O stretching. The band at 456.20  $\text{cm}^{-1}$  was assigned to Si-O-Si bending vibrations (Gadsden, 1975; Madejova, 2003).

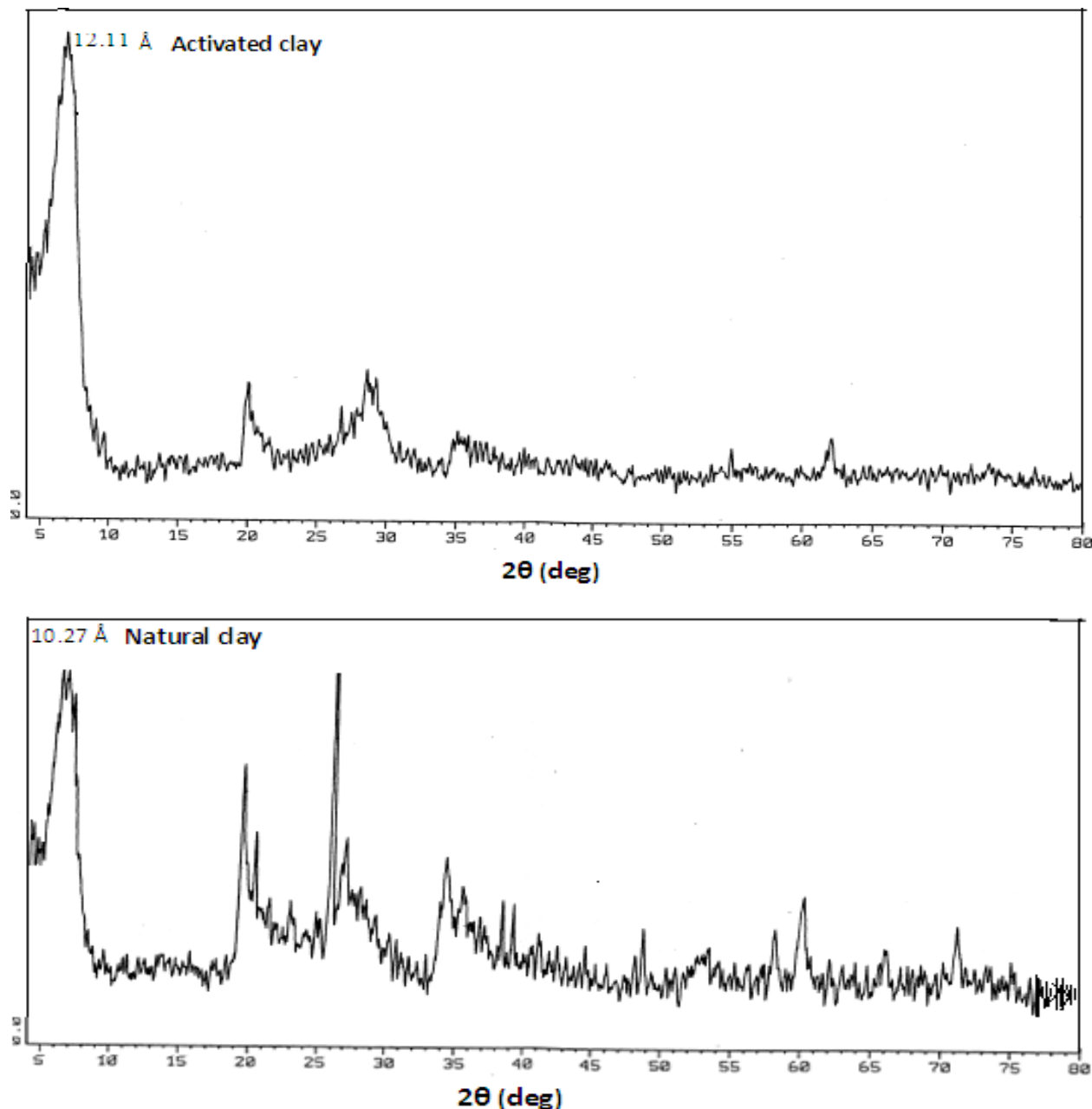
### Experimental procedure

Adsorption experiments were carried out by agitating 100 mg of natural clay with 100 ml of phenol solution of desired concentration and pH at 180 rpm, 23°C in a thermostated mechanical shaker (ORBITEK, Chennai). Concentration of phenol was estimated spectrophotometrically by monitoring the absorbance at 270 nm using UV-Vis spectrophotometer (Hitachi, model 8543).

The pH was measured using pH meter (3151 MWT, Germany). The samples were withdrawn from the shaker at predetermined time intervals and the phenol solution was separated from the adsorbent by centrifugation at 1,000 rpm for 15 min. The absorbance of supernatant solution was measured. Effect of pH was studied by adjusting the pH of phenol solutions using dilute HCl and NaOH solutions. Effect of adsorbent dosage was studied by agitating 100 ml of 5 mg/l phenol solutions with different adsorbent doses (1 to 5 mg) at equilibrium time.

The amounts of phenol sorbed by the adsorbent were calculated using the following equation (Denizli et al., 2005):

$$Q = (C_i - C_e) V/M \quad (1)$$



**Figure 1.** X-ray diffraction patterns of the natural clay and the activated clay.

Where  $Q$  (mg/g) is the amount of phenol sorbed by natural clay,  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium liquid-phase concentration of phenol, respectively,  $V$  (L) the initial volume of phenol solution and  $M$  (g) the weight of the natural clay.

The percentage amount of adsorbate adsorbed on the adsorbent was calculated by Equation (1) where  $C_i$  and  $C_e$  are the percentage adsorption was calculated using the following equation:

$$\text{Percentage (\%)} \text{ adsorption} = [(C_i - C_e) / C_0] \times 100\% \quad (2)$$

### Adsorption isotherm

#### *Langmuir isotherm model*

Langmuir model assumes that the adsorption energy is constant and independent of surface coverage, adsorption occurs on localized sites with no interaction between adsorbate molecules and maximum adsorption occurs when the surface is covered by a monolayer of adsorbate (Langmuir, 1918). The following relation represents the linear form of the Langmuir isotherm

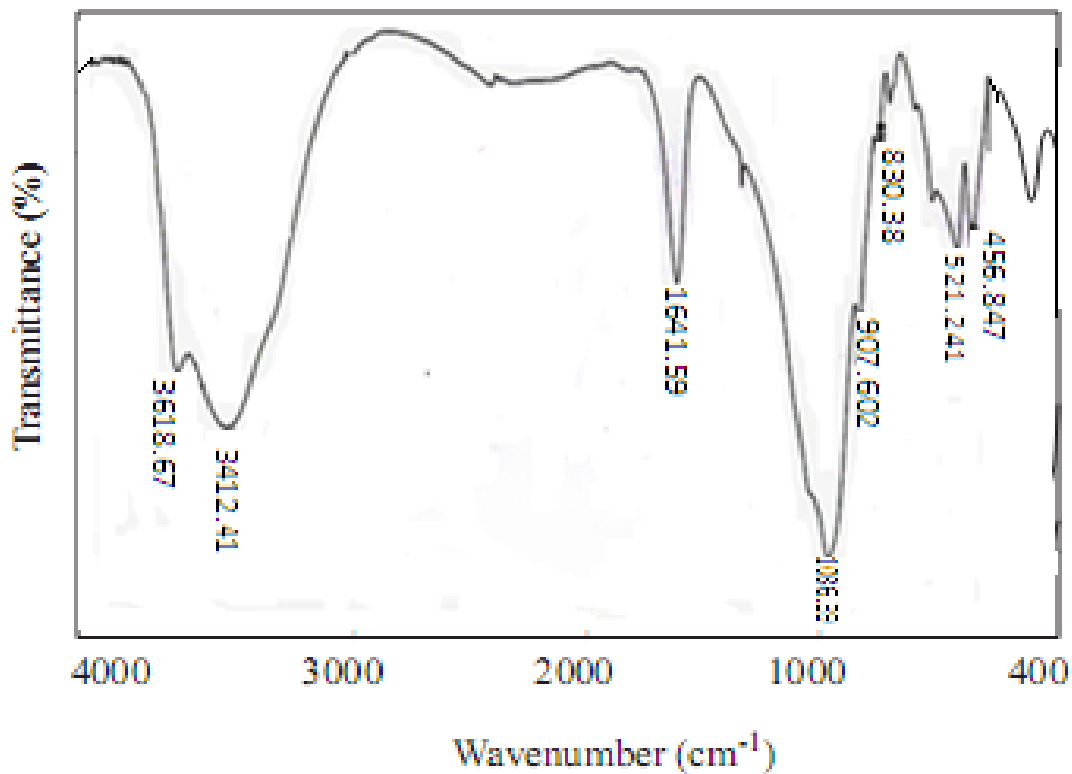


Figure 2. FTIR Spectra of activated clay.

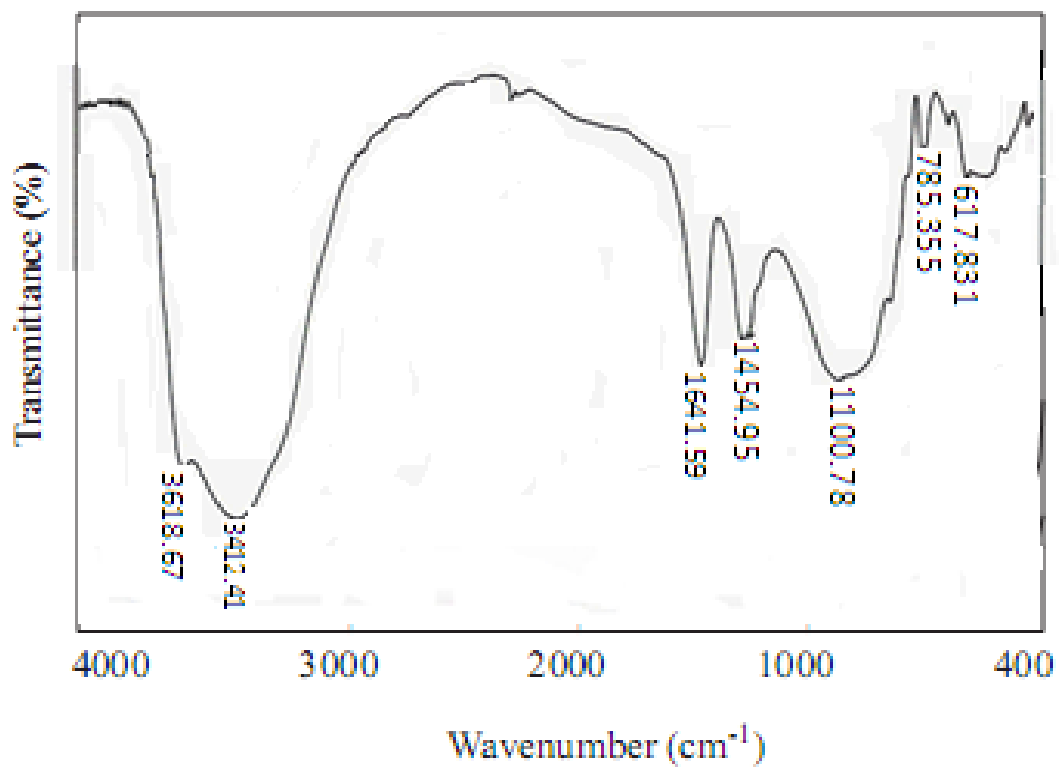


Figure 3. FTIR Spectra of natural clay.

model:

$$Q_e = Q_m \times K \times C_e / (1 + K \times C_e) \quad (3)$$

where,  $Q_e$  is the isotherm amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/l), and  $q_m$  (mg/g) and  $b$  (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of  $1/q_e$  versus  $1/C_e$  as shown in Figure 1.

### **Freundlich isotherm model**

Freundlich model is predicated based on the assumption that maximum adsorption capacity consists of a monolayer adsorption. It occupied heterogeneous adsorption surface and active sites with different energy which is unlike the Langmuir model. The linear form of the Freundlich isotherm model is given by the following equation (Freundlich, 1926):

$$\ln Q_e = \ln K_F + 1/n \ln C_e \quad (4)$$

Where  $K_F$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively of the sorbent. The values of  $K_F$  and  $1/n$  can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of  $\log q_e$  versus  $\log C_e$  as shown in Figure 2.

Based on values of correlation coefficient,  $R^2$  summarized in Table 3, the adsorption of phenol on activated and natural clay was described well by both Langmuir and Freundlich models. Both homogeneous and heterogeneous adsorption energy took place during the process. On the other hand, the Freundlich and Langmuir models were the best model to explain the adsorption behavior phenol on activated and natural clay.

The Freundlich model was the best to describe the adsorption equilibrium data at low concentrations and at different temperatures with  $R^2 = 0.999$  (Equation 4), implying the presence of highly energetic sites where the molecules of phenol were adsorbed (Bras et al., 2005). After the point of inflection of the experimental data, the Freundlich isotherm predicted that the equilibrium adsorption capacity should keep increasing exponentially with increasing equilibrium concentration in the liquid phase. However, the experimental adsorption isotherm for phenol presented a long plateau at higher equilibrium concentrations, implying the presence of a monolayer. Thus, Freundlich model should not be used for extrapolation of this data to higher concentrations. Langmuir model (Equation 3) gave a better fit at higher

concentrations (Figure 3) with a determination coefficient of  $R^2 = 0.998$  (Table 2), implying the formation of a monolayer at higher concentrations, however, the deviation of this model at low equilibrium concentrations implied that the sites of adsorption on the surface of the adsorbent were heterogeneous.

For comparison, the parameter constants for adsorption of phenol on activated clay were also listed in Table 2. Based on values of correlation coefficient,  $R^2$ , the adsorption of phenol was best fitted by Langmuir model. In addition, it was clearly seen that the adsorption capacity,  $Q_{max}$  (mg/g) for adsorption of phenol on activated clay was significantly higher than adsorption on natural clay.

Besides, the values of Freundlich constant  $K_F$  taken as an indicator of adsorption capacity was also greater for adsorption of phenol on activated clay as compared to the adsorption on natural clay.

However, natural clay still showed its feasibility and it is a promising adsorbent since it is abundantly available and cheaper than commercial activated carbon. Basically, a good adsorption by activated natural clay could be explained additionally by its high surface area (Lin and Cheng, 2002).

## **Adsorption equilibrium**

### **Effect of contact time**

Figure 3 showed the effect of contact time on the removal of phenol by natural and activated clay. For different duration of time (ranging from 0.5 to 24 h), well-shaken phenol solution (100 ml, 5 ppm) was studied for equilibrium. The study revealed 5 and 5.5 h as the equilibrium time for natural and activated clay, respectively.

Natural and activated clay were considered fast because of a rapid increase of adsorbates adsorbed occurred at the first 120 min. Previous findings on the adsorption of phenolic compounds by various clay-based adsorbents had shown a wide range of adsorption time (Wu et al., 2001).

Therefore, the result in present study was in agreement with the other reported findings. Up to 70 and 60% of phenol, respectively was successfully adsorbed by activated and natural clay from the aqueous solution. This proved the feasibility of activated natural clay as an effective adsorbent (Halouli and Drawish, 1995; Song and Sandi, 2001).

Figures 4 and 5 displayed the adsorption isotherms at 23°C, of phenol from aqueous solutions onto natural and activated clay. As could be seen, there was a marked higher adsorption for activated clay than that for natural clay, reaching a maximum value of 18.86 mg/g for activated clay, 11.01 mg/g for natural clay, respectively.

**Table 1.** Characteristic of the selected adsorbate.

Name	Formula	Molecular weight	Henry's constant (bar m <sup>3</sup> /mol)	Water solubility at 25°C (g/L)	Log K <sub>ow</sub>	Observations
Phenol	C <sub>6</sub> H <sub>6</sub> O	94	4 X 10 <sup>-7</sup>	87	1.5	Aromatic semivolatilite weak acid, pK <sub>a</sub> = 9.98

**Table 2.** Adsorption constants for adsorption of phenol on activated and natural clay at different temperatures.

Natural clay	Langmuir constants			Freundlich constants		
	Q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	K <sub>F</sub> (L/mg)	1/n	R <sup>2</sup>
T = 296°K	11.095	1.170	0.997	0.589	0.4	0.997
T = 301°K	9.107	0.849	0.998	0.381	0.73	0.998
T = 306°K	7.630	0.508	0.997	0.271	0.98	0.998
Activated clay	Langmuir constants			Freundlich constants		
	Q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	K <sub>F</sub> (L/mg)	1/n	R <sup>2</sup>
T = 296°K	18.86	1.710	0.997	0.703	0.266	0.998
T = 301°K	15.47	0.970	0.996	0.574	0.420	0.999
T = 306°K	12.51	0.586	0.940	0.456	0.594	0.998

**Table 3.** The thermodynamic parameters for the adsorption phenol on natural and activated.

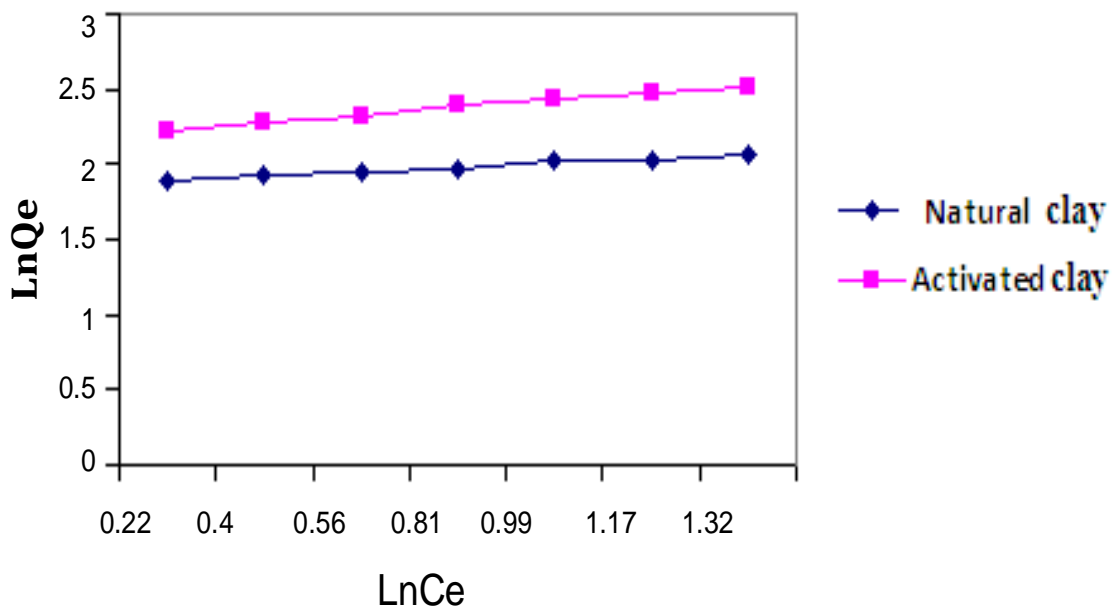
Natural clay	Thermodynamic parameters		
	ΔH° (kJ/mole) mean value	ΔG° (kJ/mole)	ΔS° (J/k mole) mean value
T = 296°K		-3.293	
T = 301°K	-1.666	-3.311	5.510
T = 306°K		-3.340	
Activated clay	Thermodynamic parameters		
	ΔH° (kJ/mole) mean value	ΔG° (kJ/mole)	ΔS° (J/k mole) mean value
T = 296°K		-2.611	
T = 301°K	-1.331	-2.632	4.339
T = 306°K		-2.652	

The maximum adsorptions capacities obtained in this work were higher than those reported by Tahani et al. (1999) for the adsorption of phenol from water onto an Al-PILC (13 mg/g) and onto an inorganic-organic clay (IOC; quaternary amine-Al PILC) (29.2 mg/g).

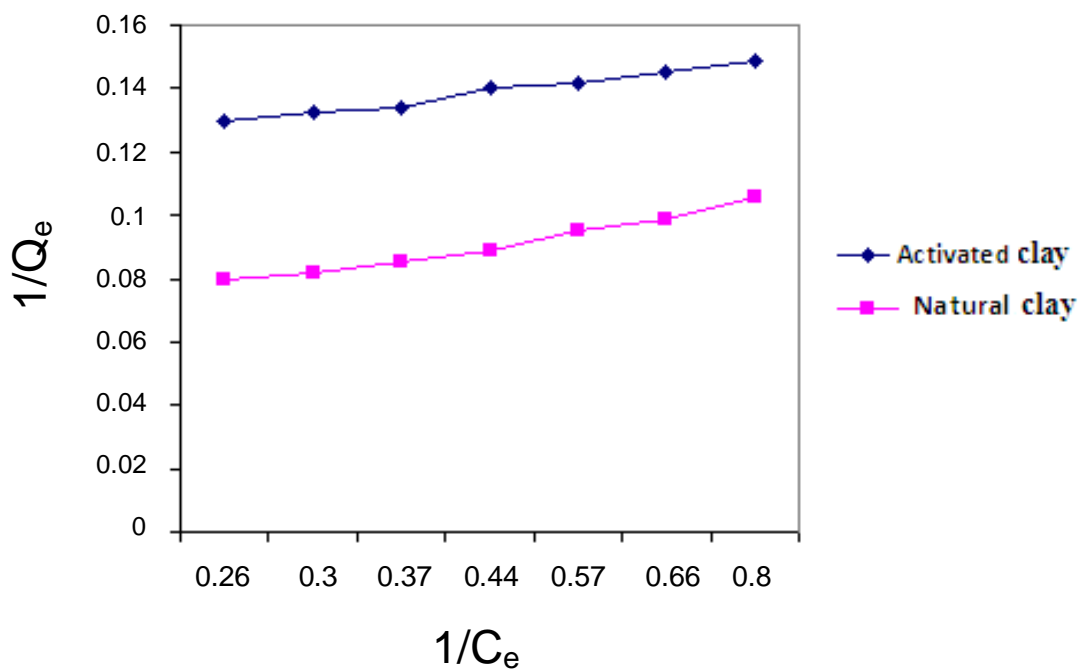
Figure 6 showed an expanded view of the adsorption isotherm of phenol in the range of 0 to 5 ppm to show in detail the initial section of the isotherm. This Figure 7 showed a sigmoidal (S-shape) that reached a long plateau as the concentration increased. This isotherm could be classified as an S2 isotherm under the (Giles et al., 1960) classification system (cooperative adsorption) based on the initial shape of the isotherm. According to

this classification in S2 isotherms, the more molecules of adsorbate were already adsorbed, the easier it was for additional amounts of adsorbate to become fixed to the surface of the adsorbent. This implied a side-by-side association between adsorbed molecules, helping to hold them to the surface and consequently making more stable the adsorbed layer.

Molecules of adsorbate that showed an S-shape isotherm (as in the case of phenol) were considered monofunctional where the attraction towards the surface of the adsorbent arose from its OH group, giving an arrangement of adsorbed molecules oriented perpendicularly to the surface. Under the experimental



**Figure 4.** Freundlich isotherms for phenol adsorption on activated and natural clay modified montmorillonite at temperature of 23°C.



**Figure 5.** Langmuir isotherms for phenol adsorption on activated and natural clay at temperature of 23°C.

adsorption conditions, the pH was in the range of 5 to 6, below the pKa of phenol (pKa = 9.89) (Table 1) and below the pKa for silica (pKa = 9.42) (Goyne et al., 2002), therefore the phenol and the silanol groups of the surface of the adsorbent, were in a protonated form, making

possible that the molecules of phenol were adsorbed onto the surface silanol groups through hydrogen bonds as illustrated in Figure 8. This mechanism was similar to that which was reported for the adsorption of phenol onto the surface of silica (Goyne et al., 2002).

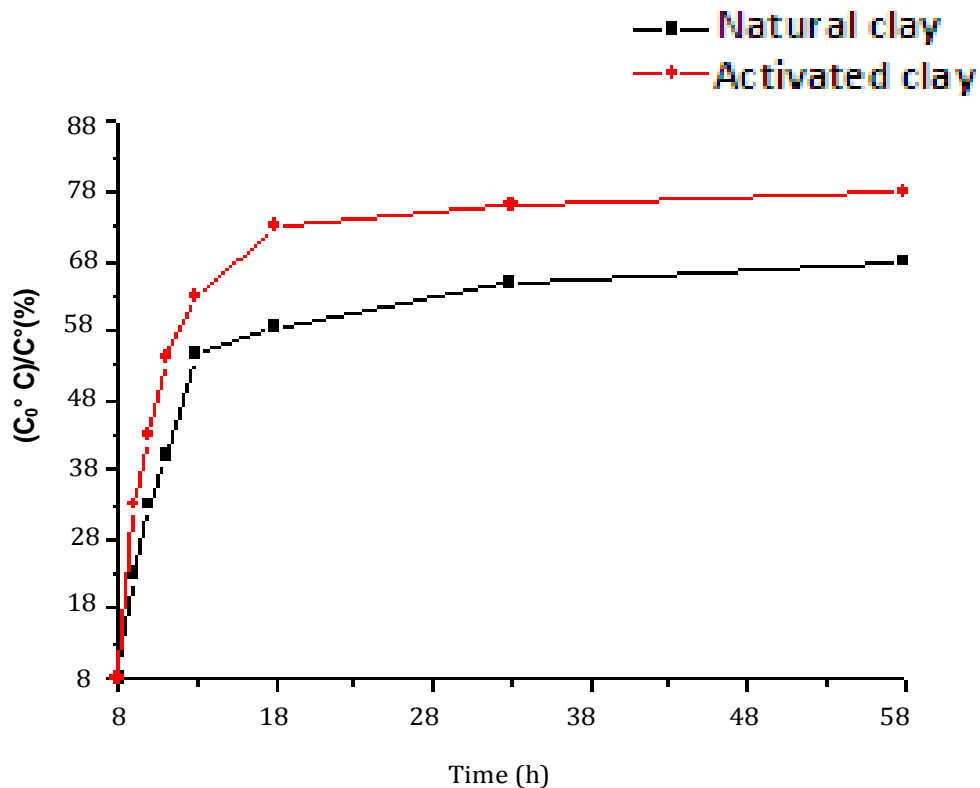


Figure 6. Effect of Time on phenol adsorption.

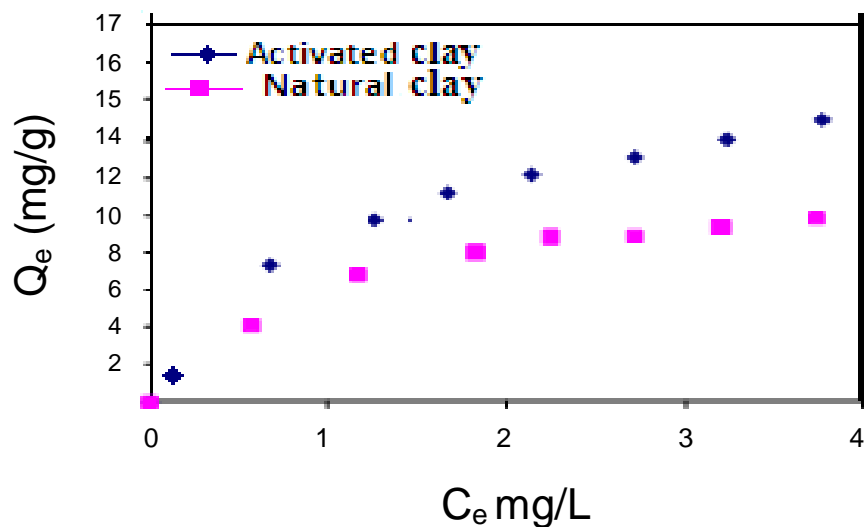


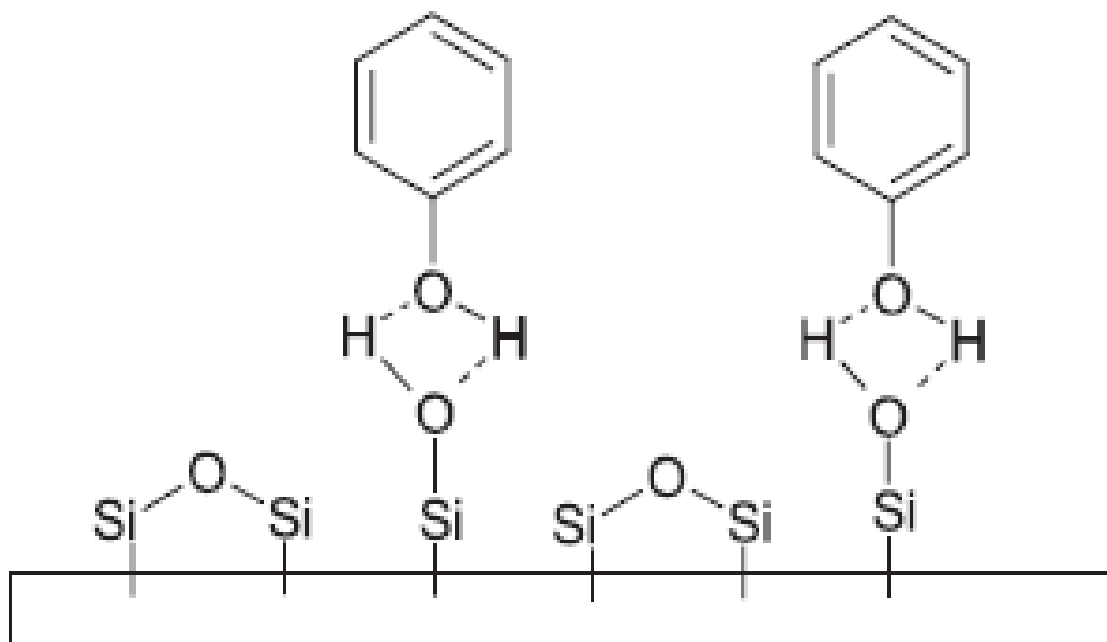
Figure 7. Sorption isotherm of phenol on natural and activated clay.

#### Effect of pH on phenol adsorption

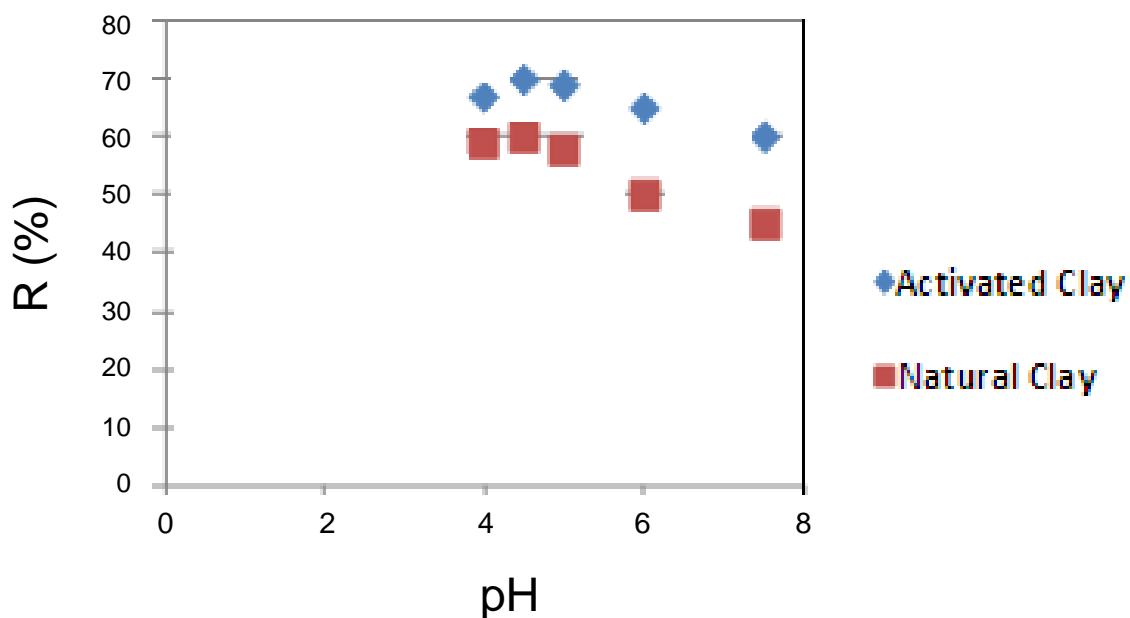
Since phenol sorption had been reported to be affected by the pH of the adsorbate (Rengaraj et al., 2002), the adsorption of phenol by natural (NC) and activated clay

(AC) were studied at various pH values of the phenol solution (100 ml, 5 ppm). The amount of phenol adsorbed showed a declining trend with higher as well as with lower pH, with maximum removal of phenol (up to almost 100% by both the adsorbents) at pH 5 (Figure 9). This





**Figure 8.** Proposed adsorption mechanism of phenol molecules onto the surface of natural clay through hydrogen bonds between OH group of the phenol and the silanol groups of the clay surface.



**Figure 9.** Effect of pH on phenol adsorption.

reduction of phenol-sorption might be because of the suppression by hydrogen ions (at lower pH), and hydroxyl ions (at higher pH) in addition to formation of various phenolic compounds at both acidic and alkaline conditions (Khalid et al., 2000; Singh et al., 1994).

## ADSORPTION THERMODYNAMICS

### Thermodynamic parameters

The thermodynamic parameters for the adsorption of

phenol by natural and activated clay such as the enthalpy change ( $\Delta H^\circ$ ), the Gibbs free energy change ( $\Delta G^\circ$ ) and the entropy change ( $\Delta S^\circ$ ) can be calculated from the variation of maximum adsorption with temperature (T) using the following basic thermodynamic relations (Seki et al., 2006; Al-kaim, 2005).

$$\Delta S^\circ = (\Delta H^\circ_{\text{ads}} / T - \Delta G^\circ / T) \quad (5)$$

$$\ln K_e = \ln C_0 = -\Delta G^\circ / RT \quad (6)$$

$$\ln K_e = \ln C_0 = \Delta S^\circ / R - \Delta H^\circ_{\text{ads}} / RT \quad (7)$$

According to Equation 7, the mean value of the enthalpy change due to the adsorption of phenol by natural and activated clay over the temperature range studied can be determined graphically by the linear plotting of  $\ln K_e$  against  $1/T$  using the least squares analysis shown in Figure 5. The mean enthalpy change can be determined from the slope of the straight line. The variation of Gibbs free energy and entropy change with temperature can be calculated using Equations 5 and 6, respectively, the results given in Table 3.

An important result obtained (Table 3) was that the Gibbs free energy ( $\Delta G^\circ$ ) was small and negative with its value decreased with increasing temperature. This indicated that the adsorption processes of Phenol by natural and activated clay could be enhanced by decreasing temperature. The values of entropy change ( $\Delta S^\circ$ ) were positive and remained almost constant with temperature. It was evident that structural changes in phenol and natural and activated clay occurred during the adsorption process. The negative values of enthalpy change ( $\Delta H^\circ$ ) showed the exothermic nature of the adsorption process of phenol by natural and activated clay.

The value of  $\Delta H^\circ$  for the adsorption was lower than 80  $\text{kJ}\cdot\text{mol}^{-1}$ , suggesting the physical nature of the sorption (Seki and Yurdakoç, 2006), that is, physisorption conducted with Van der Waals forces.

The enthalpy change ( $\Delta H^\circ$ ) of the adsorption (-1.666 and -1.333  $\text{kJ/mol}$ ) indicated physical adsorption of phenol on to natural and activated clay (ESSINGTON et al., 1994). The overall adsorption process seemed to be exothermic.

## Conclusion

Natural clay was a potential and promising adsorbent for removal of phenolic compounds from aqueous solution. The results were compared with activated clay. The adsorption of phenol on activated clay was higher than adsorption on natural clay. However, Natural clay stood as low-cost adsorbent and it showed the feasibility to remove up to 60% of phenol, respectively for initial

concentration.

The Freundlich equation agreed very well with the equilibrium isotherm also Langmuir equation gave accepted linearity. Finally, the adsorption of phenol on the natural clay surface was exothermic. The results revealed that the natural clay could be employed as adsorbent for treatment of aqueous waste streams.

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