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Removal of Phenol in Aqueous Solution Using Kaolina Mineral Clay

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ABSTRACT

Kaolina clay were tested for phenol removal as toxic liquid waste from aqueous waste water. Several experimental conditions such as weight and particle size of clay were investigated to study batch kinetic techniques, also the pH and concentration of the phenol solution were carried out. The stability of the Langmuir adsorption model of the equilibrium data were studied for phenol sorbent clay system. Infrared spectra, thermogravimetric and differential thermal analysis techniques were used to characterize the behavior of kaolina clay and kaolina clay saturated with phenol. The results obtained showed that kaolina clay could be used successfully as an efficient sorbent material to remove phenol from aqueous solution.

Key Words: Clay / Phenol / Adsorption / Natural Minerals / Toxic waste.

INTRODUCTION

Phenol and its derivatives are the basic structural unit for a wide variety of synthetic organic hazardous wastes ⁽¹⁾. Phenol has been listed as a priority pollutants by the U.S. Environmental Protection ⁽²⁾. Phenol as a weak acid has carcinogenic nature and environmental problems when found in natural water ⁽³⁾. Some characteristic techniques such as butimization, organic solvents and industrial coal production produced phenol and phenolic compounds in the waste water solution ⁽⁴⁾. There are many methods for removing phenols and its derivatives from waste waters such as oxidation, precipitation, solvent extraction and adsorption techniques ⁽⁵⁻⁸⁾. Adsorption is a well-established and powerful technique for treating domestic and industrial effluents. However, in water treatment the most widely used method is adsorption onto the surface of clay material ⁽⁹⁻¹⁴⁾. The aim of this study was to explore the possibility of using kaolina clay for removing phenol as organic hazardous waste from the aqueous waste water. The effects of various factors such as weight, size of kaolina clay, pH, temperature and concentration of the initial phenol pollutant solution were studied on the sorption capacity of kaolina clay. The analysis of adsorption equilibrium data were done using Langmuir model.

EXPERIMENTAL

Kaolina Clay Preparation:

The kaolina clay was obtained from Sinai of the eastern desert, Egypt. After being crushing with a hammer and ground in mill, the samples was sieved to produce the desired particle size fractions. The samples with a particle size ranging from (50 to 150 μm) were washed continuously and dried at 110°C in electric oven and stored. The chemical analysis of the kaolina clay is given in Table (1), indicate that silica and alumina oxides are the major constituents of clay. Data indicate that the sample consists of quartz, kaolinite, hematite and illite as a major phase. The occurrence of the above minerals has been confirmed by XRF, XRD and FTIR techniques ⁽⁸⁾.

Phenol Preparation:

Standard solutions of phenol (Mwt 94) were prepared by weighing the purified grade chemicals and dissolving them with bidistilled water for preparing stock phenol solution with $5 \times 10^{-3} \text{M}$ concentration.

Table (1): Chemical analysis of fractions of kaolina clay Sinai in weight percent.

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	LOI at 800°C
Percent by weight	51.75	31.96	0.99	0.19	0.06	2.65	12.40

Portions of these solutions were then diluted with distilled water to give the desired test samples. Batch adsorption isotherms studies were conducted by shaking 2 gm of kaolina clay with 30 ml distilled water for about 30 minutes and then adding phenol solution to reach the volume 50 ml and concentration of phenol solution will be $0.5 \times 10^{-3} \text{M}$. the covered flasks shaken for 48 hrs to reach equilibrium. Sorption studies were also conducted at different size fractions (50, 75, 100, 125 and 150 μm). pH values (2, 3, 4, 5, 6, 7, 8 and 10) at room temperature were studied. The pH of the solution was adjusted with HCl or NaOH solution by using pH meter. Blanks were run simultaneously without an adsorbent. Temperature controlled shaking thermostat was used to control the desired shaking and temperature.

After attainment of equilibrium, the samples were centrifuged and supernatant liquid was analyzed for phenol using UV-VIS spectrophotometrically Shimadzu-160 (UV-visible) at λ_{max} 296 nm.⁽¹⁵⁾ The kaolina clay and kaolina clay saturated with phenol were characterized using infrared techniques using Pye Unicam Maltson 1000 IR spectrometer in the range 4000 – 6000 cm^{-1} . The thermal analysis was carried out using Shimadzu-50. The measurements were carried out in a temperature range from room temperature up to 800°C with heating rate 20°C min^{-1} in nitrogen atmosphere.

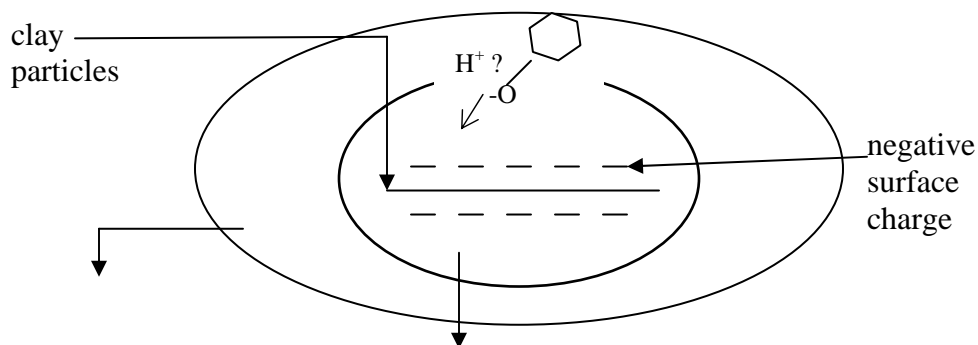
RESULTS AND DISCUSSION

The adsorption of phenol in aqueous solution on kaolina clay were examined by optimizing various physico-chemical parameters such as pH, contact time and the amount adsorbent and adsorbate.

Effect of pH:

The pH of solution has been identified as the most important variable which governs phenol adsorption on kaolina clay surface.

Fig.(1) describe the adsorption of phenol on kaolina clay at different studied pH. Figure showed maximum adsorption in neutral range (5-8) while at either very high or low pH values no adsorption was observed. As shown in the suggested clay water structure at pH >8 it may be attributed that the clay particles have active sites from (SiO₂, Al₂O₃) bearing negative charges formed from continuous shaking with water before phenol adsorption⁽¹⁸⁾, while phenol as a weak acid (PKa=10) and at this high pH value, the abundance of OH⁻ ions there by increasing hindrance to diffusion of phenol ions and also increasing electrostatic repulsion between the negatively charged particles preventing phenol adsorption.



viscous water

absorbed water
Suggested clay water structure at pH > 8 ⁽¹⁸⁾

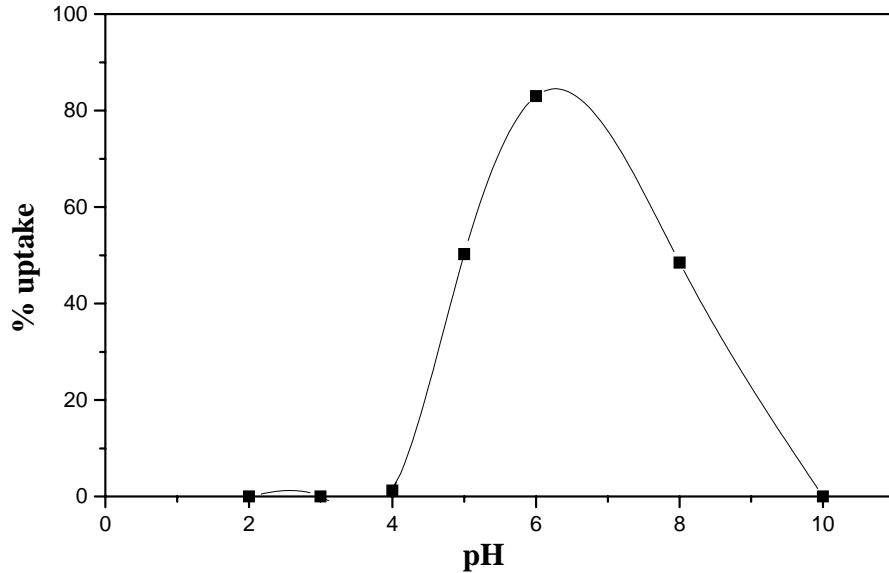
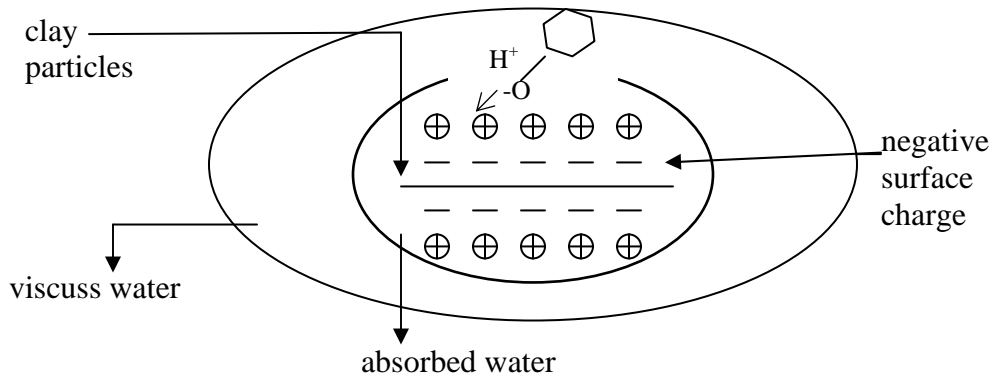


Fig.(1): Effect of pH on the removal of phenol percent by kaolina clay (dosage 2 g / 50 ml - concentration) of phenol $0.5 \times 10^{-3} \text{M}$) after 48 h.

As shown in the suggested clay water structure at pH <5, the surface of the negatively sorbent kaolina clay surrounded by the hydronium ions from the acid medium which enhance the phenol adsorption on the surface of kaolina clay. So the adsorption of phenol from aqueous solution is pH dependent and a maximum phenol adsorption was observed at pH (6 – 7) neutral medium ⁽¹⁰⁾.



Suggested clay water structure at pH < 5 ⁽¹⁸⁾

Effect of Contact Time:

The adsorption data for the uptake of phenol versus contact time at $0.5 \times 10^{-3} \text{M}$ initial concentration with 2 gm of kaolina clay were carried out at different pHs (5, 6, 8). The results show that the equilibrium time required for the adsorption of phenol on kaolina clay starts after 24h and reaches about 83% at pH equal 6 after 48 h and reach complete removal of phenol after three days at pH= 6 and after 4 days at pHs equal 5 and 8. Fig.(2) shows the effect of contact time on the removal of phenol by kaolina clay. The kinetics of phenol adsorption follows the first order rate expression at pHs 5, 6 and 8. The very slow initial adsorption of phenol on kaolina clay was attributed to the adsorption of water molecules on the negative aluminum and silicon oxides produced from shaking before starting experiment. The followed maximum uptake was carried out up to 48 h due to the replacement of adsorbed water by phenolic group.

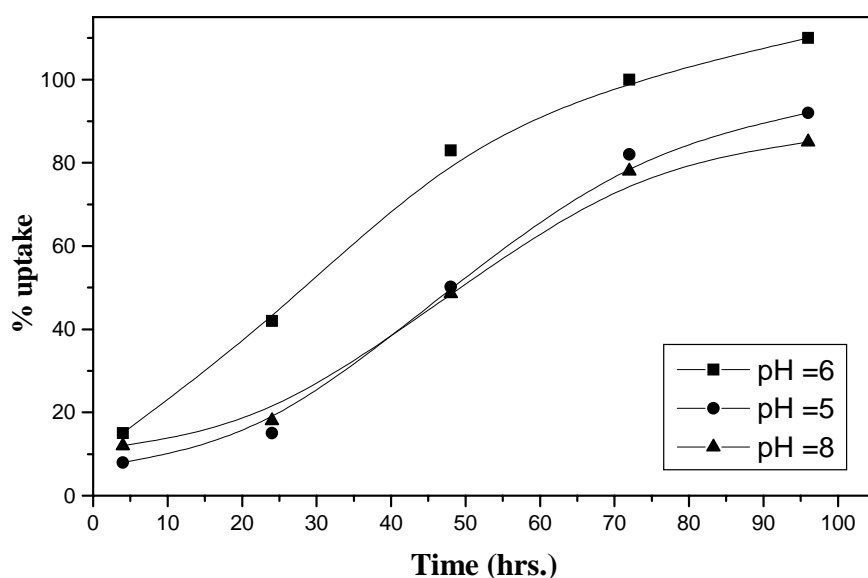


Fig.(2): Effect of contact time for removal of phenol percent by kaolina clay (dosage 2g / 50 ml - concentration of phenol $0.5 \times 10^{-3} \text{M}$.)

Effects of Adsorbent Amount:

The amount of adsorbent kaolina clay was also studied. Fig.(3) shows the removal of phenol by kaolina clay at the phenol solution pH=6. Adsorbent dosage was varied from 0.5 up 3 gm. The results show that for removal of $0.5 \times 10^{-3} \text{M}$ phenol in 50 ml solution, a minimum dosage of 2 gm of kaolina clay is required for 83% removal of phenol after 48 h, and as the adsorbent amount increase the removal of phenol increase.

Effect of Initial Phenol Concentrations:

Fig.(4) shows the influence of changing of initial phenol concentration on the uptake percent of phenol by 2 gm of kaolina clay. The results indicate that as then initial phenol concentration increase over than $0.5 \times 10^{-3} \text{M}$, the phenol removal percent of the studied clay

decreased. The equilibrium sorption capacities of phenol per one gram of kaolina clay as sorbent was calculated according to the equation:

$$Capacity = \frac{\% \text{ uptake}}{100} \cdot \frac{C_o V}{m}$$

where C_o : initial concentration g/l
 V : volume of solution in ml
 m : weight of sorbent kaolina clay.

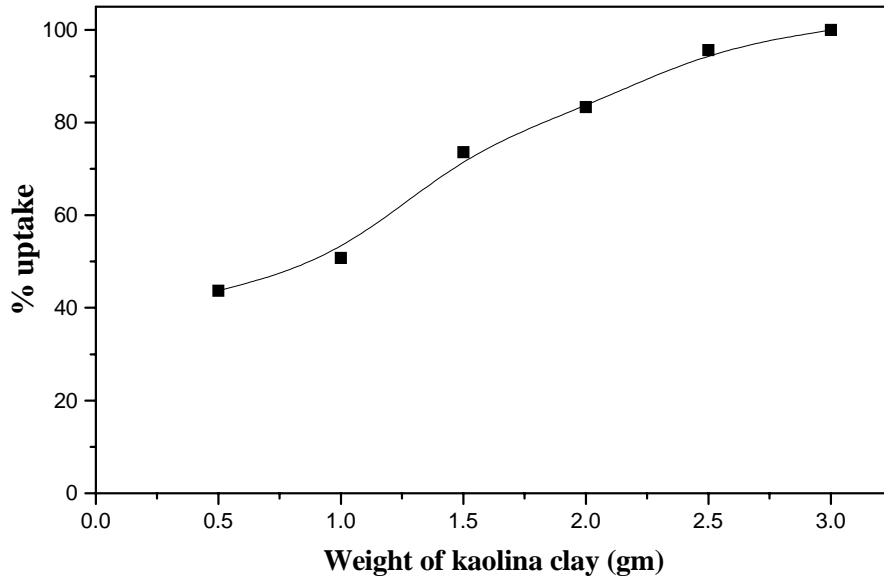


Fig.(3): Effect of kaolina clay weight on the removal of phenol percent (dosage 50 ml phenol, concentration $0.5 \times 10^{-3} M$, after 48 h at particle size $100 \mu m$.)

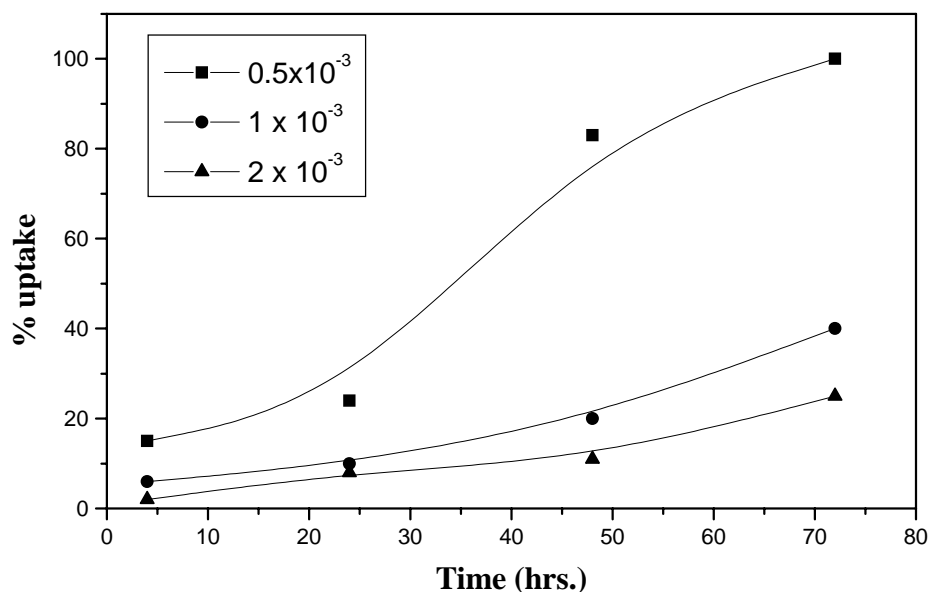


Fig.(4): Effect of kaolinite clay on the removal of phenol percent for various initial phenol concentration. [dosage : 2 gm clay - 100 μ m].

The experiment was done three times for the same 1 gm of kaolinite clay and cumulative uptake was calculated by using 0.5×10^{-3} M phenol solution. The maximum uptake was 250% and the uptake stop. On calculating the maximum capacity of 1 gm was 0.0625 gm phenol per one gram of kaolinite clay. As shown from literature the odour threshold for phenol in water has been reported to be 0.0079 g/l and taste threshold was 0.003 g/l in water ⁽²⁾.

Effect of Particle Size:

Experiments were conducted with samples having five different average particle sizes for kaolinite clay ranging from 50, 75, 100, 125 and 150 μ m in order to determine the effect of particle size on the uptake of phenol percent, as shown in Fig.(5). The uptake percent for phenol on kaolinite clay reaches maximum at particle size 100 μ m while the other particle sizes give lesser uptake phenol percent due to the optimum surface area at 100 μ m.

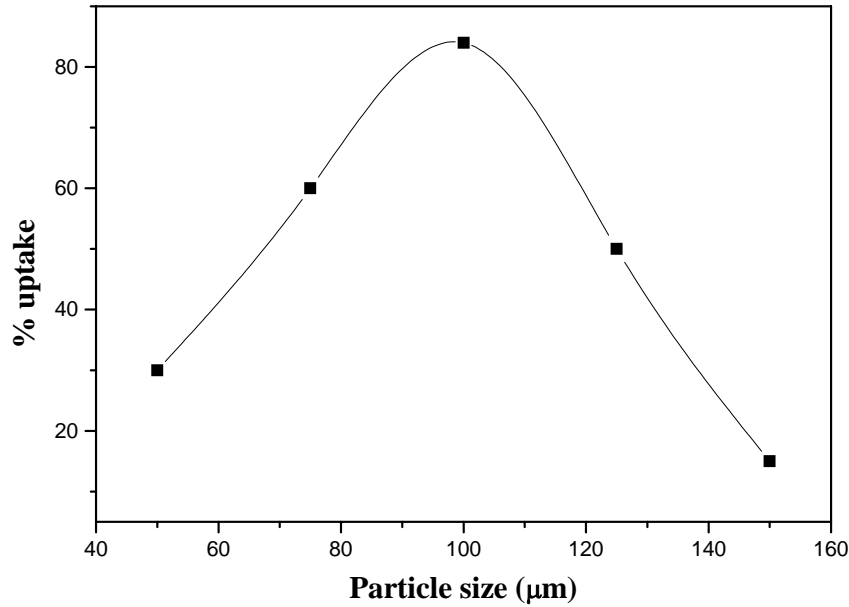


Fig.(5): Effect of particle size of kaolina clay on the removal of phenol percent (dosage: 2 gm clay - 50ml phenol,) concentration $0.5 \times 10^{-3} \text{M}$, after 48 h.)

Adsorption Isotherm Modelling:

The mathematical modelling and representation of the adsorption data is well studied. Fig.(6) and Table (2) show the adsorption isotherm graph of the amount of the adsorbed phenol against the equilibrium concentration at a specific temperature. The nature of interaction between the kaolina clay and phenol adsorbed can be determined from Langmuir isotherm⁽³⁾. The model is applicable in cases where only one molecular layer of adsorbate (phenol) is formed at the adsorbent (clay) surface. Monolayer adsorption is distinguished by the fact that the amount adsorbed phenol reaches a maximum value at moderate low concentration, this corresponds to complete coverage of the adsorbent surface (clay) by monomolecular layer of adsorbate (phenol) which remain constant after 48h. The Landmuir equation can be represented by the well known equation⁽⁴⁾;

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e$$

where, C_e and q_e are the solution (mg dm^{-3}) are surface concentration (mg.dm^{-3}) for phenol clay respectively. K_L and a are the isotherm constants for a particular (solute-solvent) condition. K_L can be determined from the interception of a plot of C_e/q_e versus C_e . The constant a is related to the energy of adsorption. The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless factor R_1 ⁽⁵⁾;

$$R_1 = \frac{1}{1 + K_L C_o}$$

$$= \frac{1}{1 + 0.11 \times 0.005}$$

$$\therefore R_1 = 1$$

where C_o is the highest initial phenol concentration ($\text{mg}\cdot\text{dm}^{-3}$). The magnitude of the R_1 factor indicates the nature of the interaction and the isotherms type as $R_1 = 1$ (linear isotherm).

The linear form of the Langmuir isotherm can be compared in ^(4,5). Results in Fig.(6) show that Langmuir model can adequately describe the adsorption data of phenol on kaolina clay.

Table (2): The linearized Langmuir adsorption isotherm for phenol with kaolina clay.

Time (h)	C_o	C_e	$q_e \cdot (C_o - C_e)$	C_e/q_e
4	0.5	0.365	0.150	2.33
10		0.325	0.175	1.80
20		0.290	0.210	1.40
30		0.200	0.300	0.66
40		0.125	0.375	0.33
48		0.085	0.415	0.20

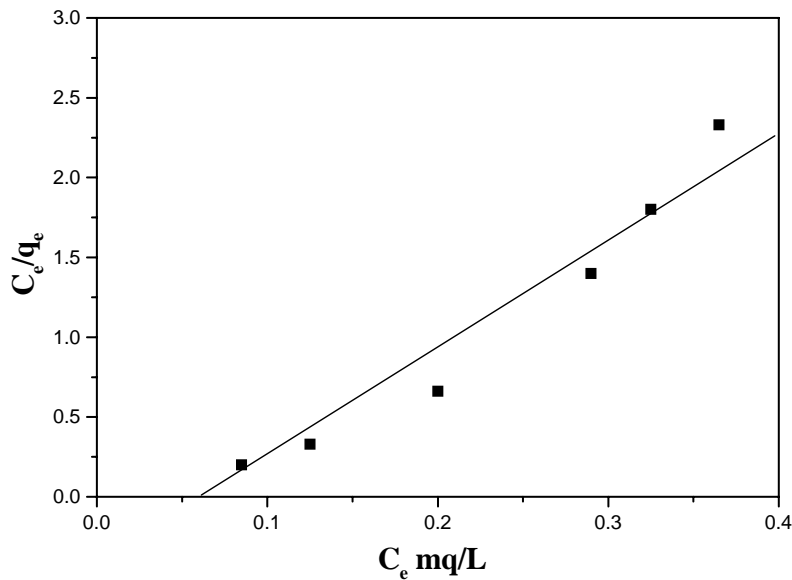


Fig.(6): The linearized Langmuir adsorption isotherm for phenol with kaolina clay.

IR Characterization:

Understanding the mechanism of phenol adsorption onto kaolina clay infrared technique was used to evaluate the mechanism involved. IR offers some indication of the ability of phenol

to react with SiO_2 and Al_2O_3 which spread over the kaolina clay surface. Fig.(7) shows the IR spectra of kaolina clay and phenol adsorbed on kaolina clay. The vibration of Si – O bond results in a band at 3700 cm^{-1} , together with a doublet, due to O – H deformation at approximately 800 cm^{-1} ⁽¹⁹⁾. The main adsorption bands of kaolina clay occurs at 3690, 1113, 1047, 910, 789 and 714 cm^{-1} . After adsorption of phenol

Thermal Analysis:

Thermal analysis supplemented by thermogravimetry TGA and differential thermal analysis DTA for kaolina clay and kaolina clay saturated with phenol. The DTA curves of these samples are shown in Fig.(8). The most striking feature of the DTA curves is a sharp endothermic peak at about 50.70°C . This low temperature peak reflects the release of interlayer water. The TG measurements are in good accordance with the results gained by X-ray analysis⁽⁸⁾. These samples show few amounts of inter layer water. The TG curves Fig.(9) show small but significant differences in three steps. The first step from the start temperature up to 100°C due to the release of interlayer water⁽²⁰⁾. The amount of released water varies between (3 – 4)% weight loss. Between 100 and 450°C only slight mass loss percent was observed. In studying the DTA the next deflection is a rather broad endothermic peak ranged from 450°C occurring maximum peak at $530\text{--}800^\circ\text{C}$. This peak was originated by non isothermal release of OH from kaolina and kaolina saturated with phenol. On studying the TG curves from $450\text{--}800^\circ\text{C}$, an enhanced mass loss percent again takes place, most probably generated by a raised release of OH from the structure of kaolina clay⁽²¹⁾. The mass loss at this step $450\text{--}800^\circ\text{C}$ is clearly reduced pointing to an increased dehydroxylation of the kaolina. The amount of mass loss varies between (4.9 – 9.0)% weight loss. Altogether the mass loss was 7.67% for kaolina and 13.5% for kaolina saturated with phenol.

CONCLUSIONS

- Kaolina clay is an effective adsorbent for removal of phenol from aqueous solutions at pH equal 6 and reaches 100% after three days.
- Phenol sorption capacity by kaolina clay was improved by selecting the particle size and weight of the kaolina clay.
- The maximum loading capacity of phenol per one gram clay was 0.0625 gm.
- The equilibrium data have been analyzed for phenol – clay system using Langmuir isotherm and provide the best correlation due to the monolayer adsorption.

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