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RESEARCH ARTICLE

A Thermodynamic Study of Adsorption 2-(4-Antipyriyl azo) Orcinol [APAO] on Zincoxide as Adsorbent

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Abstract

We can remove Organic materials contaminated from their solutions in several methods, for examples the Adsorption. In this research was studies adsorption APAO which dissolved in 2.5% ethanol/water by the Zinc Oxide as adsorbent. The adsorption isotherms it was found similar to L4-shape according to Gilles classification. Also it studied the influence of adsorbent weight and adsorption time on removal% of APAO; it was 0.35gm best weight and 35 min. best time. The impact of changing the function of the acidic PH on removal% of APAO was found as follows (PH=4> PH=10> PH=7). The thermodynamic values were calculated (ΔH, ΔG, ΔS) depending on changing temperature with concentration were (+24.74002KJ/mol, +9.4256KJ/mol, +51.390J/mol.K).

Introduction

In our days we Faces a major challenge to solve the problems of environmental pollution, especially water pollution [1].The wastewater resulting from various industrial processes and especially from the factories that use organic materials (dyes) in dye the textiles and other tools represents a serious risk to the general population because of the poor biodegradability, high toxicity, and potential accumulation in the environment [2].

Therefore, the need arises to invent ways to expel these contaminants and channel the water to be drinkable. One of these ways were adsorption process, which can be defined as the first step in any chemical reaction, it is defined as substance pooling (Atoms, Ions or molecules) called Adsorbate on the surface of another substance called Adsorbent. Usually escorted the adsorption diminution in Free energy and Entropy because the adsorbates become restricted by associated with adsorbent. So lose part from the degree of freedom, accordingly Enthalpy is degrees by (ΔG =ΔH - TΔS).

Factors Affecting on Adsorption

- **Nature of the Adsorbent** (solid):

(I) Porous and soft powder steel: Overall, Porous and finely powdered solid for instance fullers earth, coal, adsorb more In comparison with the hard non-porous materials. Because of this feature gas masks are used charcoal powder.

(ii) Surface area of the adsorbent depends upon its particle size, i.e. Adsorption capacity increases by increasing the surface area of the adsorbent (the smaller the particle size) .

- **Adsorption Concentration:**

The adsorption direct proportion with the concentration.

- **Effect of Pressure:**

The adsorption direct proportion with pressure at constant temperature.

- **Effect of Temperature:**

If the adsorption is endothermic, temperature direct proportion with the adsorption, but temperature reverse proportion with the adsorption if exothermic.

- **Effect of Acidity Function:**

The effect different from compound to another, depending on the nature of adsorbent and adsorbate.

Types of Adsorption

There are two types from adsorption: Physical adsorption and Chemical adsorption.

Difference between them:

Chemical adsorption	Physical adsorption
- Heat of adsorption is more than 80KJ/mole. - Molecules are held due to chemical bond forces. - Single-layer consists from adsorbate on adsorbent. - Activate energy are appreciable. - It is very specific and selective in nature.	- Heat of adsorption is less than 40KJ/mole. - Molecules are held due to vanderwaal's forces. - Several layers consist from adsorbate on adsorbent. - Activate energy are small. - No specific

Adsorption Isotherm

Adsorption is usually described through Isotherm, that is, the graph between the amount of adsorbate on the adsorbent and concentration at constant temperature. Gilles researcher a rating system for adsorption isotherm depending on the initial sections to isotherms, It is (S, L, H, C).

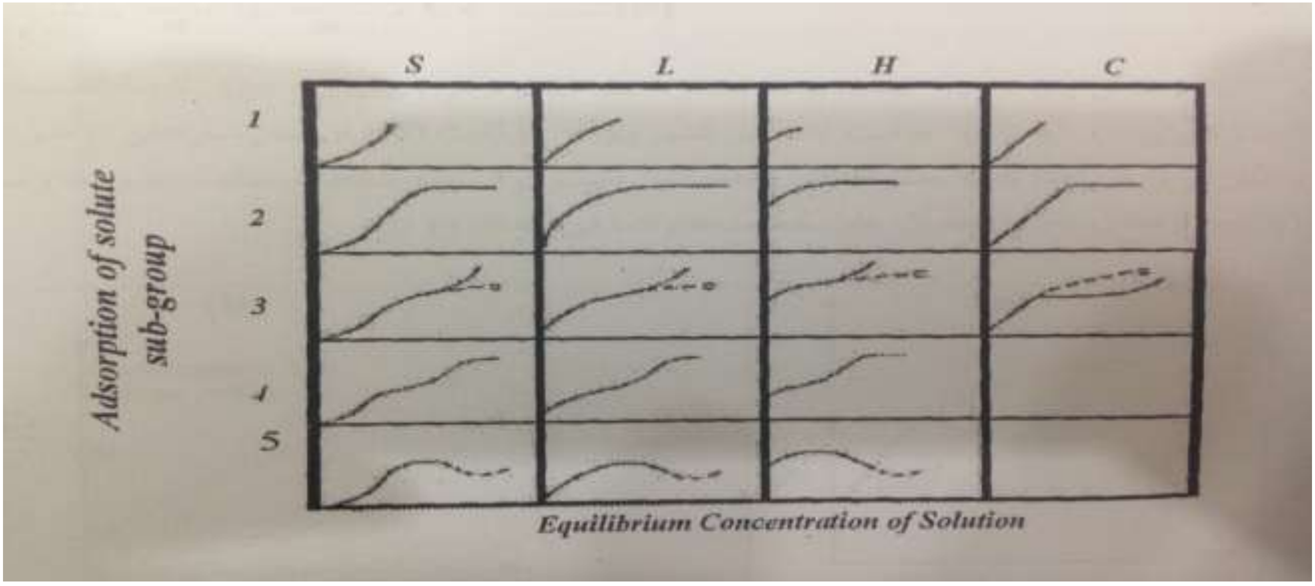

Figure 1: show the Gilles classification to adsorption isotherm

Material

- **Adsorbent: Zinc oxide**

Chemical formula ZnO is an inorganic powder, it does not dissolve in water, and its color is white and molecular weight equal to 81.408 g /mole. Its uses are extensive as an additive too many materials for example glass, plastics, ceramics, cement, rubbers, lubricants [8].

- **Adsorbate: [APAO] 2-(4-Antipyriyl azo)Orcinol** [9]

The Chemical formula of APAO [$C_{18}H_{26}N_4O_3$] and the Molecular Weight equal to 346 g/mole. The chart below shows the steps to prepare the APAO:

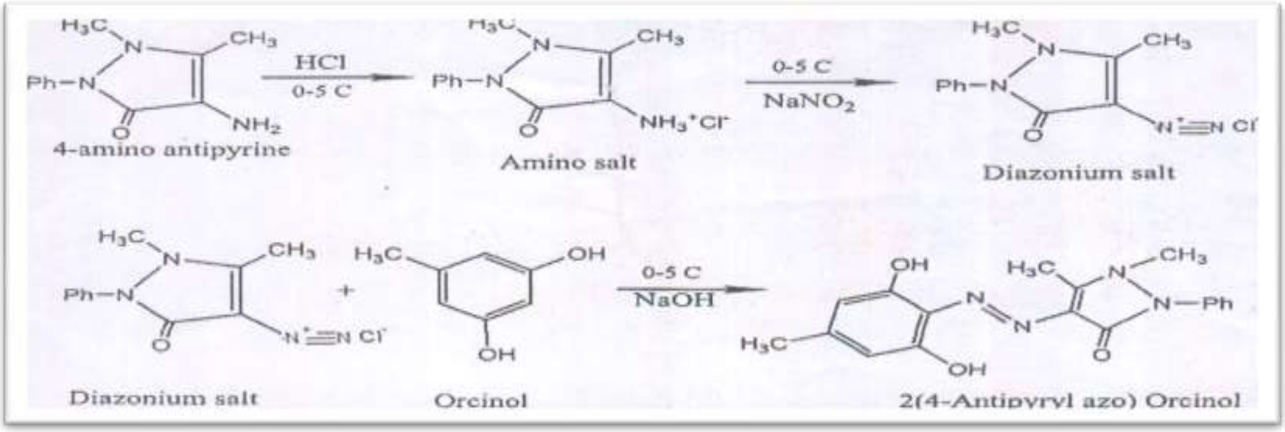

Figure 2: show the steps to prepare the APAO

- **NaOH and HCl**: to change the acidic function of the solutions.

Methods

- Determine the greatest wavelength :

By the electronic scanning spectroscopy was measured the greatest wavelength, within the range (200-780 nm).It was equal to 430nm.

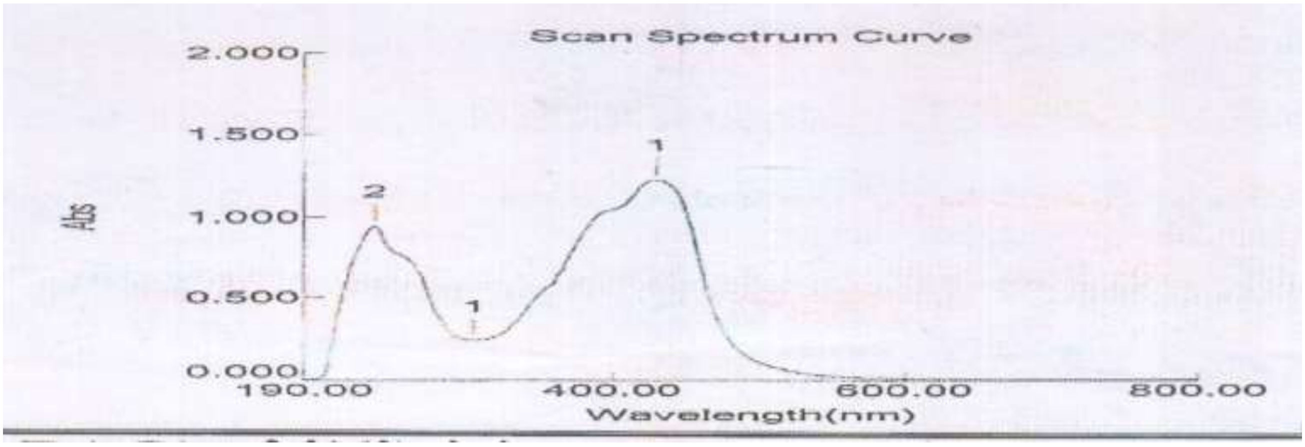

Figure 3: show the greatest wavelength of APAO

- Calibration curve of APAO:

The five concentrations prepared within the range (20-100ppm) to draw calibration curve between concentration and absorption for each concentration.

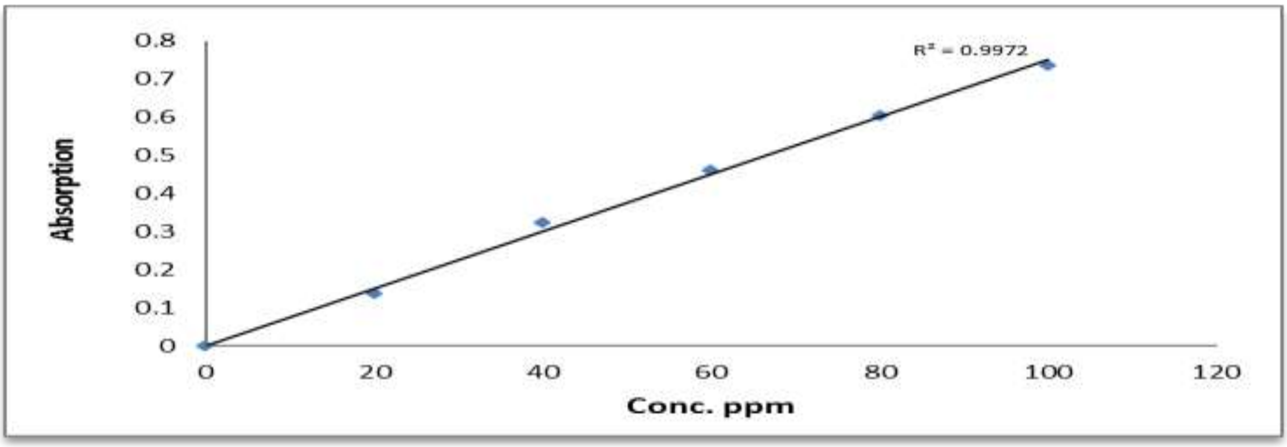

Figure 4: show the Calibration curve of APAO

- **Effect of Time**

For the purpose of determining the best time for adsorption were taken ten beakers and put in all of them (20ml) of APAO with concentration (60 ppm) in contact with the (0.3gm) of zinc oxide and then placed in a water bath (298K) and then was pulled first beaker after five minutes and measured absorption and so for the rest of beakers (be checked out after every 5 minutes) to the extent of fifty minutes, it was noted that the best time was (35min).

- **Effect of Weight:**

For the purpose of determining the best weight for adsorption were taken ten beakers and put in all of them (20ml) of APAO with concentration (60 ppm) in contact with the different weights of zinc oxide and then placed in a water bath (298K) for (35min) and then was measured absorption and so for the rest of beakers to the extent of 50 minutes, it was noted that the best weight was (0.35gm).

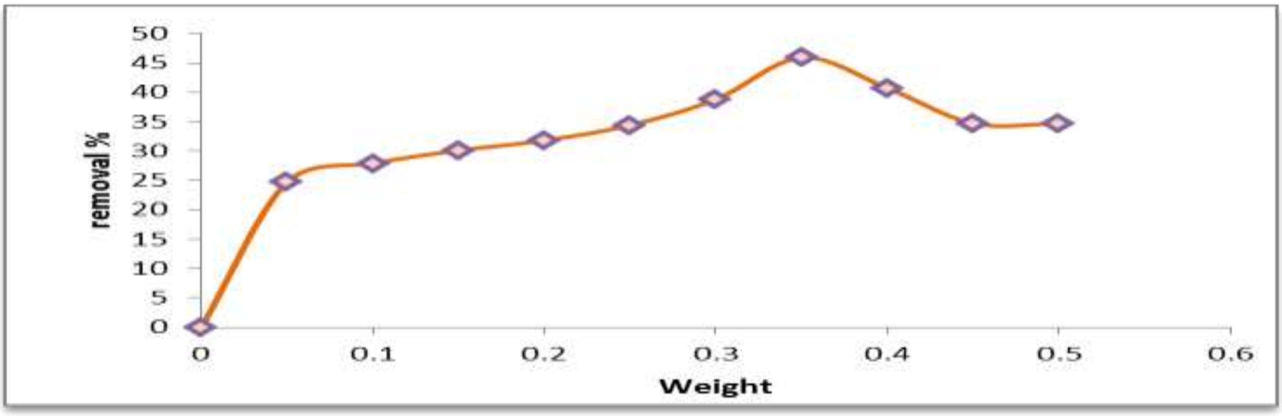

Figure 5: show the effected the removal% of APAO by weight

Result and Discussion

Figure (6) show the adsorption isotherm of the APAO at 298k by zinc oxide as adsorbent. The removal% increased with increase APAO concentration [10].The removal% was calculated by equation:

$$\text{Removal\%} = \frac{A_0 - A_{abs}}{A_0} * 100$$

A_0 : The absorption of initial concentration before adsorption (C_0 ppm).

A_{abs} : The absorption of initial concentration after adsorption.

The adsorption isotherms it was found similar to L4-shape according to Gilles classification.

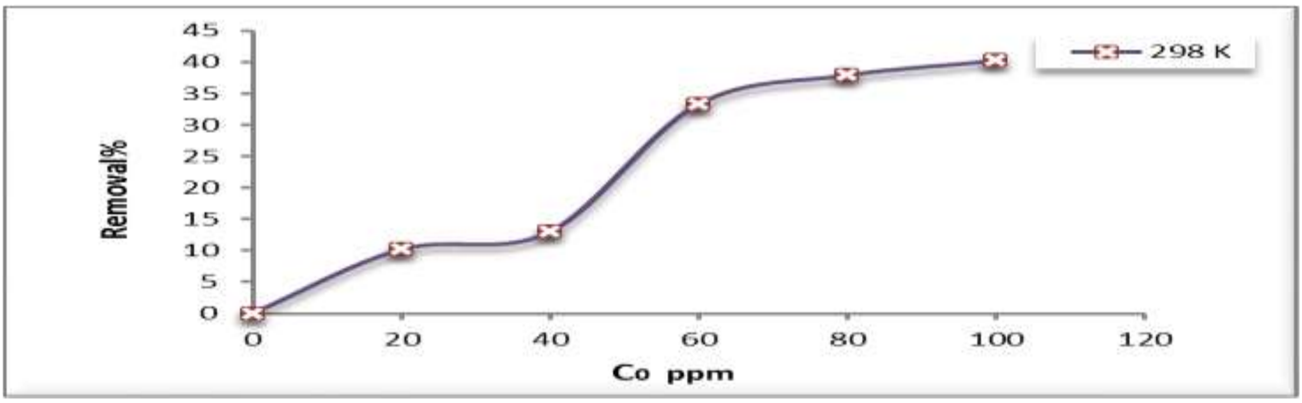

Figure 6: show the adsorption isotherm of the APAO at 298k

Two main theories have been adopted to describe adsorption isotherms. The first, Langmuir isotherms which represented by the linear equation:

$$Ce/Qe = 1/a + (b/a)\ Ce$$

Where a: represents a piratical limiting adsorption capacity when the surface is fully covered with a monolayer of adsorbate, the constant b: is the equilibrium adsorption constant which related to the affinity of the binding sites [11].

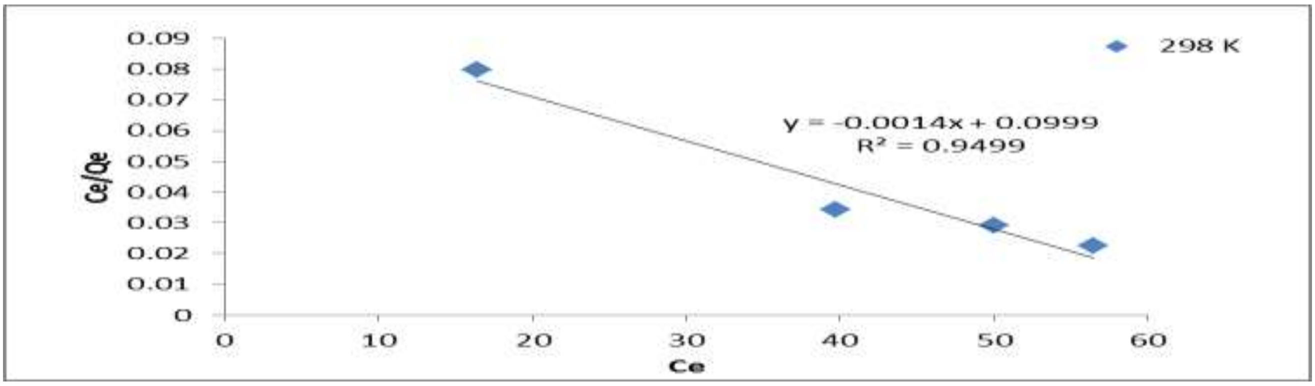

Figure 7: Linear form of Langmuir equation for the adsorption of APAO on ZnO surface at 298K and PH=7

The applicability of these equations on the adsorbent-adsobate (solute) system assume the formation of one layer of adsorbate molecules on the surface while the Freundlich adsorption isotherm (equation) consider heterogeneity of the surface and the formation of more than one layer is probable.

The linear form of freundlich isotherm is Log Qe = Log K_f + (1/n) Log Ce Where (K) and (n) are Freundlich constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively [12].

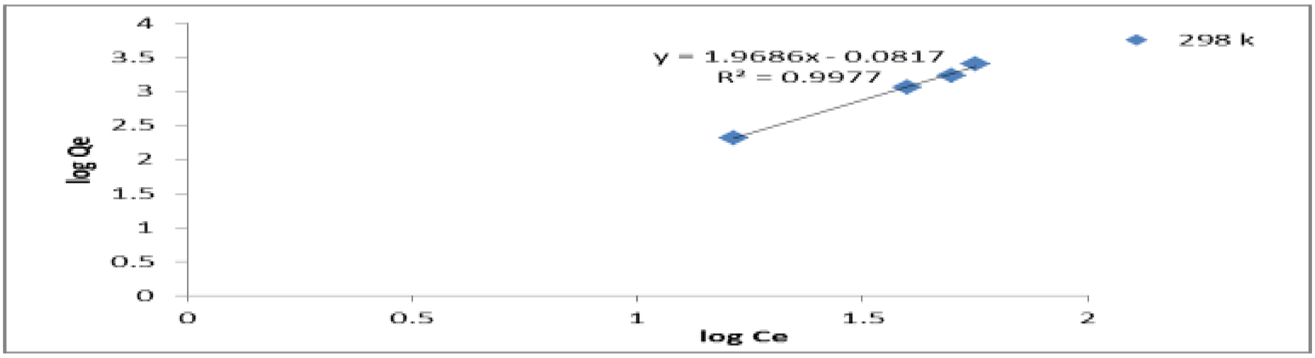

Figure 8: Linear form of Freundlich equation for the adsorption of APAO on ZnO surface at 298K and PH=7

Table: Langmuir and Freundlich isotherm constant

Compound	Freundlich constant			Langmuir constant		
	K_f	n	R^2	a	b	R^2
APAO	1.2069	0.5079	0.9977	10.01	-0.014	0.9499

Effect of Temperature

Adsorption isotherms were taken for the APAO in the temperature range (298-328 K).

The Figure (9) show the result, the adsorption was Endothermic process because the removal% is increase with high temperature.

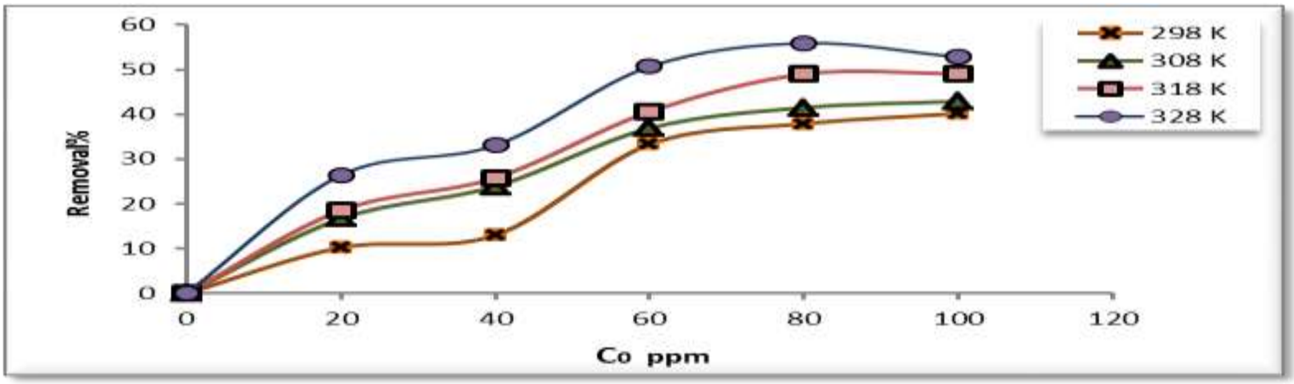

Figure 9: show the effected the removal% of APAO by Different Temperature at PH=7

At drawing logX_m value Opposite 1/T value as in Figure (10) can be calculated the ΔH value by the slope of the line product depending on the equation log X_m = - ΔH / 2.303 RT, and then calculate ΔG, ΔS by the equations ΔG = RT ln X_m/C_e ,ΔS = (ΔH - ΔG) /T the thermo dynamical parameters values are:

Dye	ΔH KJ.mol-1	ΔG KJ.mol-1	ΔS J.mol-1.K-1	Constant
APAO	+24.74002	+9.4256	+51.390	7.5508

The positive value of free energy change indicates a non-spontaneous adsorption process [13].

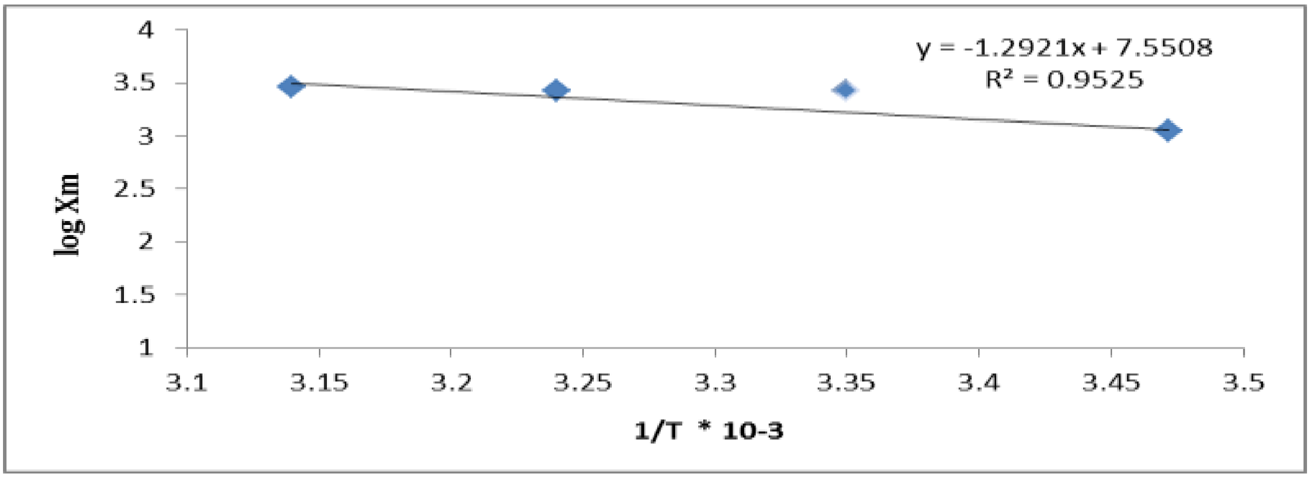

Figure 10: show the modified Vant Hoff's equation for the adsorption APAO on the ZnO at different temperatures

Effect of pH

To study the effect of hydrogen ion concentration (pH) on adsorption of APAO by adsorbent ZnO, at different values of the function acidic (pH=4, 7, 10) and (298k). The removal% was found as follows (PH=4> PH=10> PH=7) as show Figure (11).

From the figure can note the removal% of APAO increase in pH=10 because the base pulls hydrogen ions from the APAO to acquire a negative charge and thus increasing the proportion link the APAO with adsorbent.

And more increase removal% in pH=4 because the increasing number of positive ions in the acidic solution that is geared toward groups in APAO, so more likely occurrence of hydrogen bonds between these groups with adsorbent [14].

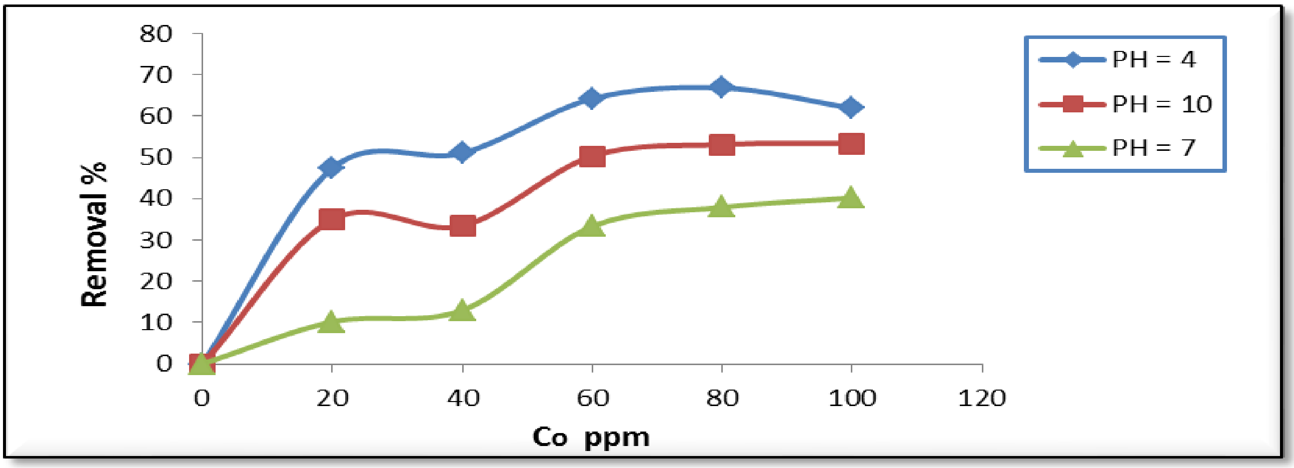

Figure 11: show the effect of PH on the removal% of APAO at 298k

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