

# Kinetic and Equilibrium Studies on the Adsorption of Albumins on Charcoal Derived From Almonds Shell

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## ABSTRACT

In this research, the activated charcoal derived from almonds shell was found to have a good non conventional adsorbent used for the adsorption of Bovine serum albumin (BSA) and egg white albumin (EWA). In the present study pH=6 of BSA and contact time of 80 min as well as EWA of pH =2 and contact time of 80min. The effect of doses shows that activated charcoal from almonds shell of 0.2 g for BSA, EWA respectively. The effect of temperature and thermodynamic functions were also studied and found that the adsorption ratio decrease with increase the temperature and the reactions was exothermic and spontaneous. After fixing the best conditions for the adsorption. The results were analyzed by the Langmuir, Freundlich equation using linearized correlation coefficient, the pseudo first order rate equation by Lagergren was tested on the kinetic.

**Keywords:** Adsorption, isotherms, BSA, EWA

## 1. INTRODUCTION

Many fundamental studies in the last few years have dealt with the adsorption behavior of proteins on surface<sup>1,2</sup>. Protein adsorption plays a vital role in determining the nature of the tissue implant interface, since the adsorption of proteins can significantly affect biomaterial surface properties between as blood coagulation and cell adhesion<sup>3</sup>.

The interaction between biomolecules, such as proteins and cells, and biomedical device is a common phenomenon in vivo. It has been shown that the surface charge, topography, wettability and chemistry can have influences on protein adsorption process. Well known methods to determine the protein adsorption include ultraviolet (uv) spectroscopy<sup>(4,5,6)</sup>. Proteins are the most abundant macromolecules in biological cells. The function of a protein molecule is decided by its space structure to a great extent, so the change of the specific space structure might cause the forfeiture of its function, even the death of whole cell<sup>(7)</sup>. Serum albumin, the most abundant protein in the circulatory system, has been one of the most extensively studied proteins. In our work, bovine serum albumin (BSA) is selected as our protein model because it is well suited to these initial studies and has been extensively characterized<sup>(8)</sup>. BSA is a single-chain 582 amino acid globular nonglycoprotein cross-linked with 35 cysteine residues (17 disulfide bonds and 1 free thiol). BSA has a wide range of physiological functions involving the binding, transport, and delivery of fatty acids. It is divided into three linearly arranged, structurally distinct, and evolutionarily related domains (I, II and III); each domain further divided into two sub domains. BSA possesses two tryptophan's Try-134 and Try-214: Try 134 located in proximity of the protein surface<sup>9,10</sup>. Eggs are used in baked cereal products because of their nutritional and functional properties<sup>11</sup>. Egg white has been successfully used in the food industry as the major foaming protein, this is possible due to the ability of the egg white to have homogeneous foams of great volume, while improvement of the foam stability in the presence of the other compounds or heating, therefore the use of egg white in ceramics shape forming has many advantages in the porous ceramic processing, egg white is non toxic, biodegradable, cheap and widely available<sup>(12)</sup>.

In this work the adsorption of EWA, BSA from aqueous solution on charcoal derived from were evaluated by UV-Visible spectrophotometer.

## 2. EXPERIMENTAL

### 2.1 Materials and Instruments

1. Bovine serum albumin were supplied by Sigma Chemical Co.
2. Spectrophotometer T604, pg, Instruments, LTD
3. Balance sensitive –W-Germany
4. pH-meter HANNA, Portugal
5. Oven memmert, Edelstahi, Germany
6. Shaker Bath, Indicator GCA, Chicago
7. Centrifugal, Herouse, septch

### 2.2 Preparation of Charcoal Derived

The charcoal derived used in this study was prepared by pulverizing the walnut shell and peach Nuclei into the powder in the laboratory pulverizing, washed and dried in oven. It was then kept in furnace up to 600°C for two hours<sup>13</sup>.

### 2.2 Preparation of Albumine Solution

A standard stock solution of albumine (200ppm) was prepared by dissolving (0.04gm) Bovine serum albumine and Egg white albumine in (200ml), the volumetric flask 200ml was completed to the mark with distilled water which was

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contained 200mg/L of albumines. Solution of different concentration were prepared by serial dilutions for range (10-100mg/L).

### 2.3 Albumine Adsorption on the Surface

All results analytical were carried out on a UV.-visible spectrophotometer (Shimadzu) and used 1cm quartz cell. Batch adsorption experiments were carried out in a series of volumetric flasks of 50ml capacity and added 0.05g of charcoal derived from shell with 20ml of the aqueous albumins solutions in the room temperature it put the water bath shaker for determined time interval at a constant speed of 180rpm. Then was filtered and the residual amount of albumins were determined. Spectrophotometry by depending on Bear-Lambert law.

The amount of albumins retained by surface was calculated from the relation<sup>14</sup>.

$$Q_e = \frac{(C_o - C_e)V}{m}$$

Where:-

$C_o$  = is the initial concentration (mg/L)

$C_e$  = is the equilibrium concentration (mg/L)

$V$  = is the total volume of albumines (L)

$M$  = is the weight of surface (g)

$Q_e$  = is the amount of adsorption (mg/g)

In this research on the effect of contact time, weight of adsorbent, PH, temperature, volume of solution.

## 3 RESULTS AND DISCUSSION

### 3.1 Adsorption Isotherm

Equilibrium studies that give the capacity of the adsorption and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium is shown Fig-1. The earliest and simplest known relationships describing the adsorption are the freundilsh and the Langmuir isotherm<sup>15</sup>.

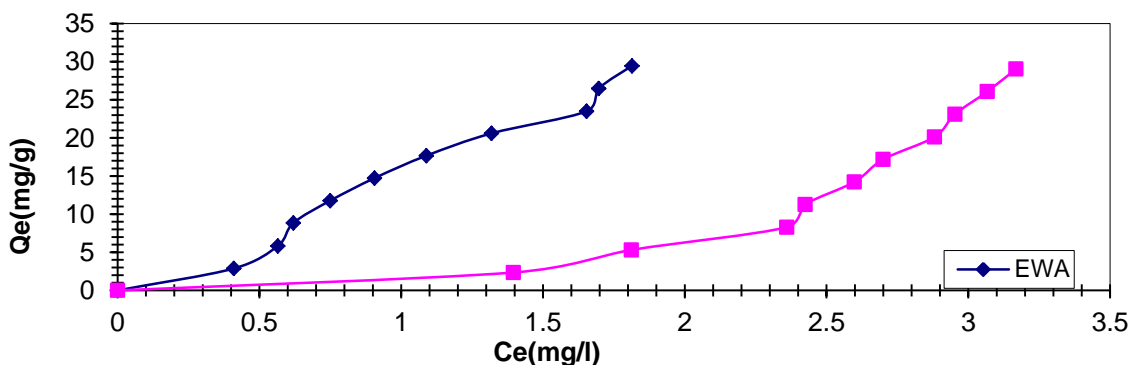


Fig-1: Adsorption isotherms of albumine on charcoal derived from almonds shell

The Langmuir of albumin on surface. The following equation can be used to model the adsorption isotherm<sup>(16)</sup>Fig-2.

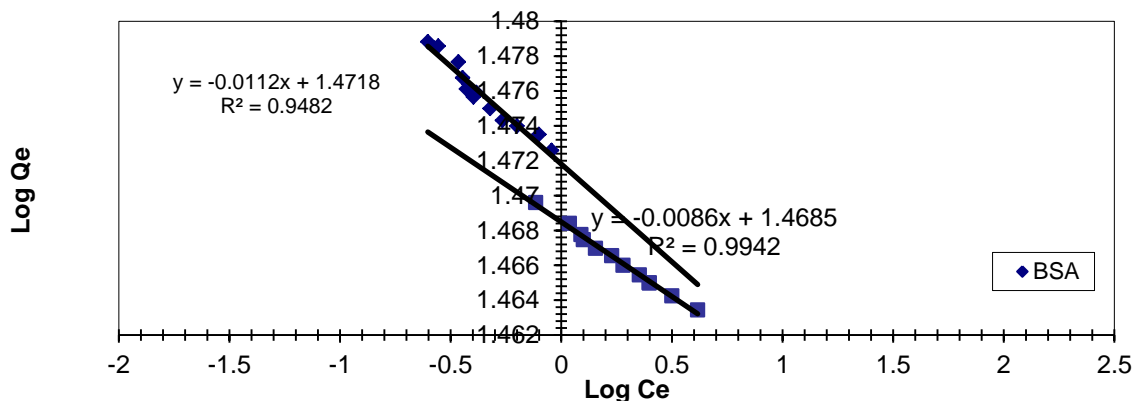


Fig-2: Linear Freundlich for adsorption albumine on charcoal derived from almonds shell

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a}{K_L} \cdot C_e$$

Where:-

Ce = is the equilibrium concentration (mg/L)

Qe = is the amount of adsorption (mg/g)

a, K<sub>f</sub> from intercept and slope respectively are shown on Table-1.

The freundlich isotherm was chosen to estimate the adsorption intensity of the adsorbent towards the adsorbent. The linearised form of freundlich adsorption isotherm was used to model<sup>17</sup> Fig-3.

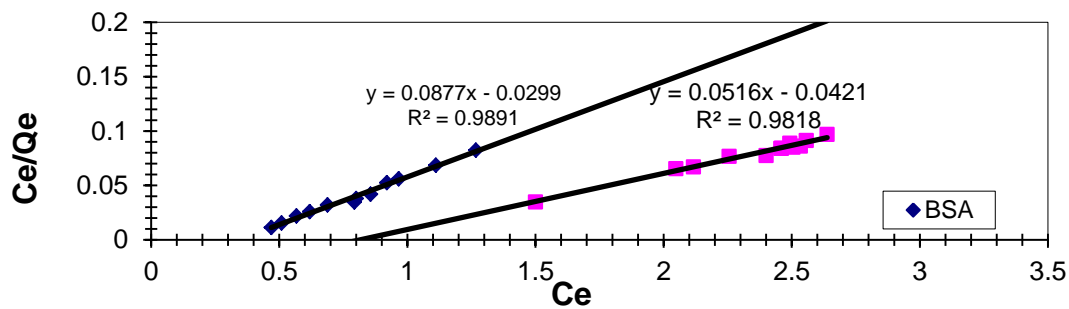
**Table-1:** Freundlich and Langmuir isotherms for albumin using charcoal derived at 303K

albumin	K <sub>f</sub>	N	R <sup>2</sup>	a	k	R <sup>2</sup>
BSA	29.648	89.28	0.9482	1.000	11.403	0.9891
EWA	29.417	11.627	0.9942	0.999	19.379	0.9818

$$\text{Log } Q_e = \log K_f + \frac{1}{n} \log C_e$$

Where:-

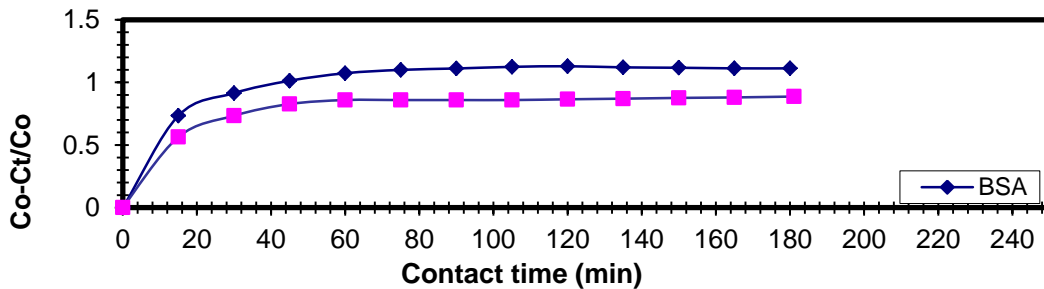
K<sub>F</sub>,n are calculated from the intercept and slopes of the freundlich plots respectively are shown Table-1



**Fig-3:** Linear Freundlich of albumine on charcoal derived from almonds shell

### 3.2 Contact Time Effect

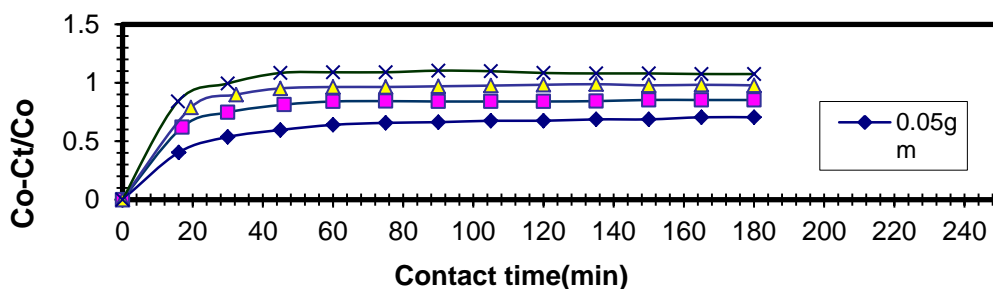
From Fig-4 indicate that adsorption efficiency increased with on increase in contact time before equilibrium is reached. The maximum contact time of BSA on charcoal derived from almonds shell was reached within 80 min, while EWA in 80 min greater availability of various functional groups on the surface of charcoal derived, which are required for interaction with anions cautions, significantly improved the binding capacity and the process proceeded rapidly<sup>18</sup>.



**Fig-4:** Effect of contact time for albumine on derived charcoal from almonds shell

### 3.3 Weight of Adsorbent Effect

Effect of adsorbent weight change on adsorption process of the charcoal derived from almonds shell has been studied by using affixed concentration of EWA, BSA and different weight (0.05,0.1,0.15,0.2) in shown Fig(5,6)the curves increasing the adsorbent weight with contact time of shown the higher amount of the adsorbent in (0.2mg) of BSA, EWA.



**Fig-5:** Adsorption of BSA on charcoal derived from almonds shell in different weight

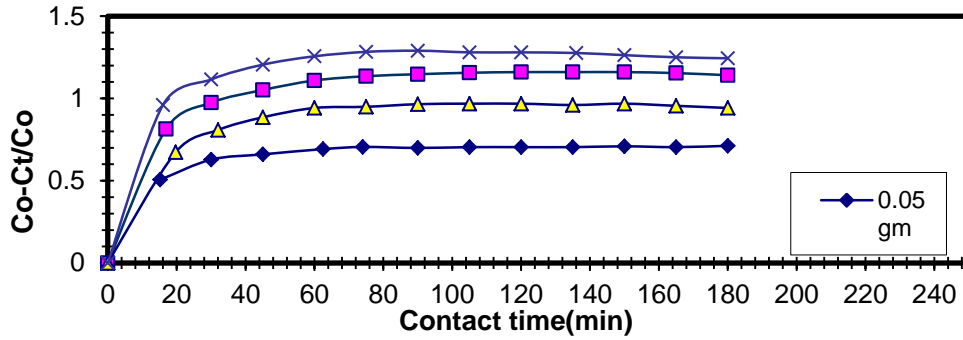


Fig-6: Adsorption of EWA on charcoal derived from almonds shell in different weight

### 3.4 pH Effect

Fig-7 shows the effect of pH on the adsorption of BSA, EWA on charcoal derived from almonds shell by rang (2-14). The amount of adsorption is maximum at pH=2 of EWA, and pH=6 of BSA. The system is strongly pH dependent, because the properties of both the charcoal derived and the solution composition of albumin changes with pH<sup>19</sup>.

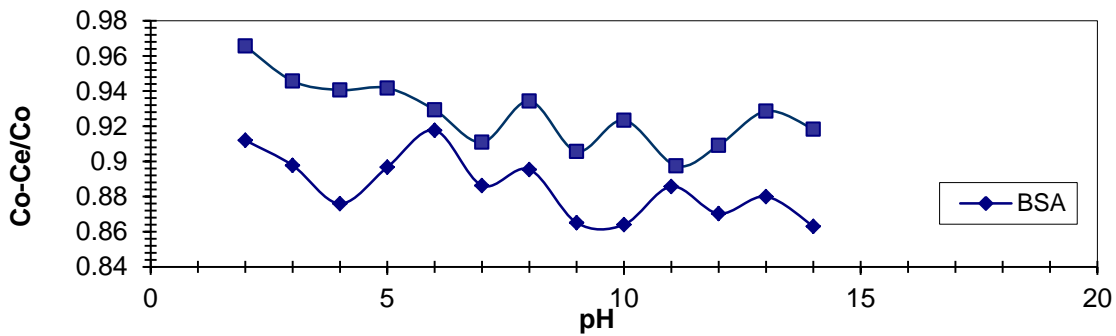


Fig-7: Effect of PH for albumine on charcoal derived from almonds shell

### 3.5 Initial Concentration Effect

The initial adsorbate concentration provides an important driving force to overcome all mass transfer resistance of albumine between the aqueous and surface<sup>20</sup>. Fig (8,9) clearly shows that the albumine amount adsorption increase with increasing adsorbate initial concentration. The reduction in albumine amount adsorption may be ascribed to the fact that the number of action adsorption sites to accomodate adsorbate albumin remains constant but with increasing adsorbate concentration. This may be due to the increase in the number of albumines competing for the available binding sites in the surface of the adsorbate.

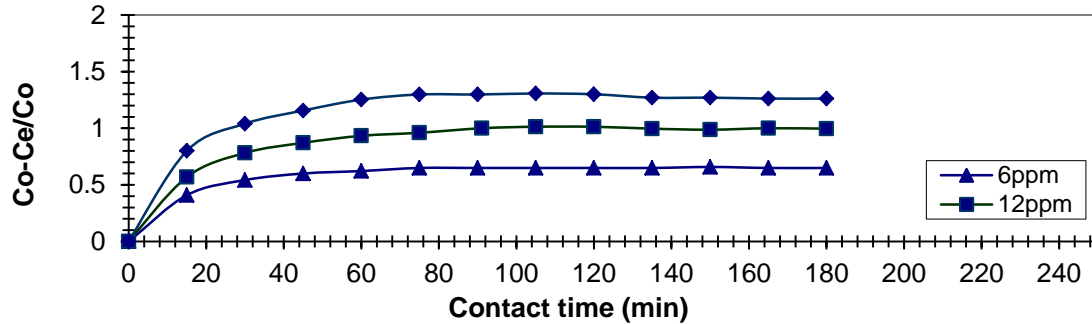


Fig-8: Adsorption of BSA on charcoal derived from almonds shell in different solution

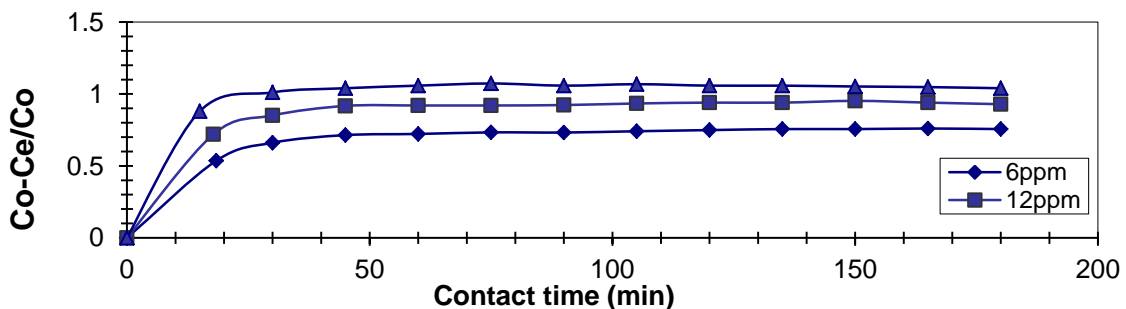


Fig-9: Adsorption of EWA on charcoal derived from in different solution

### 3.6 Temperature Effect

The effect of temperature on the adsorption extent of albumines on surface has been studied Fig (10, 11), illustrate date and general shapes of albumines adsorption at (303,313,323K). The amount of adsorption decrease with increase in the temperature the adsorption process appeared exothermic.

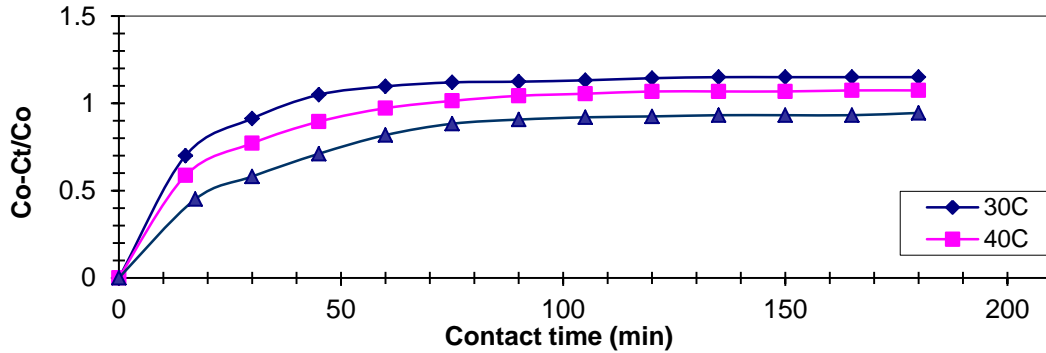


Fig-10: Adsorption of BSA on charcoal derived from almonds shell in different temperature

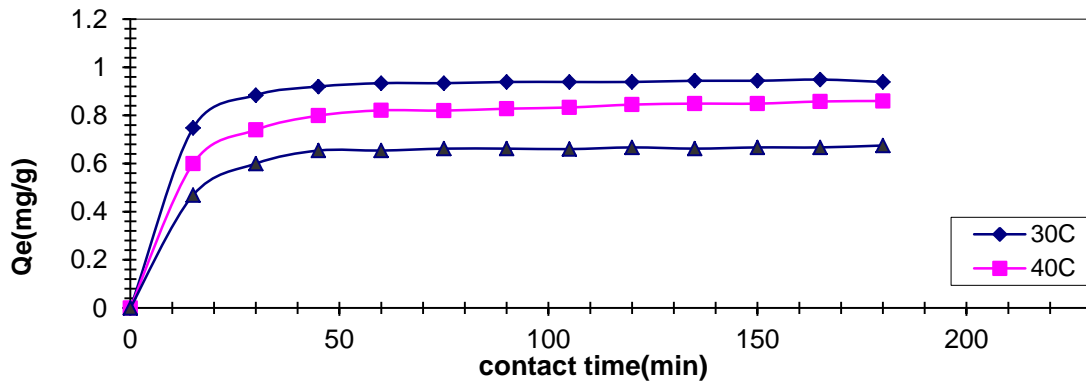


Fig-11: Adsorption of EWA on charcoal derived from almonds shell in different temperature

Thermodynamic parameters such as in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy were calculated using the following equation<sup>21,23</sup>.

$$\text{Log } X_m = \frac{-\Delta H}{2.303RT} + \text{Constant}$$

$$\Delta G = -RT \ln \frac{Q_e}{C_e}$$

$$\Delta G = \Delta H - T\Delta S$$

$Q_e, X_m$ : is the optimum amount of adsorption ,

$C_e$ : is the concentration at equilibrium

$T$ : is the temperature is (k)

$R$ : is gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{k}^{-1}$ )

The  $\Delta H$  value obtained from the slope of vant Hoff plots have presented in Table-1 and Fig-12.

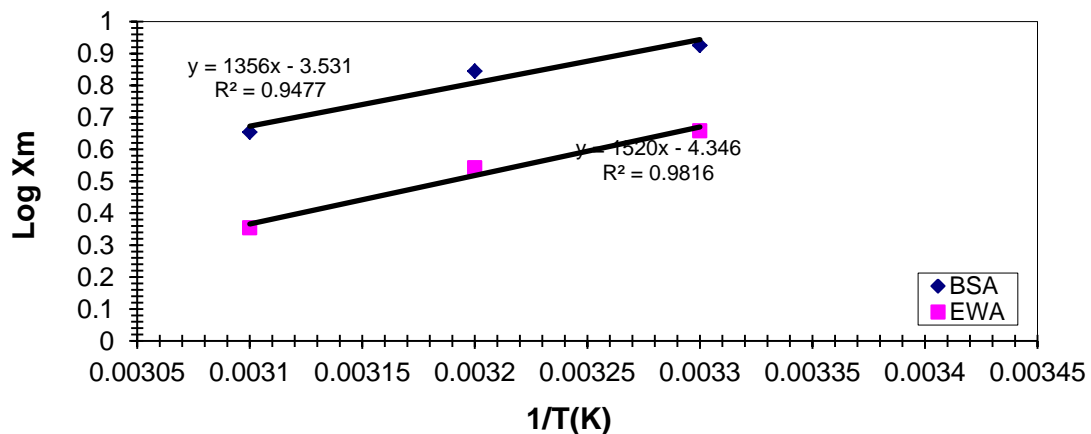


Fig-12: Relation between log  $X_m$  and  $1/T$

### 3.7 Kinetic Modeling

The kinetic of adsorption by charcoal derived from almonds shell has been tested for pseudo order equation is expressed:

$$\text{Log}(q_e - q_t) = \log q_e - K_1 t / 2.303$$

Where  $q_t$  and  $q_e$  are the adsorption capacity at time,  $t$  at equilibrium, respectively, and  $k_1$  is the rate constant of pseudo first order ( $\text{min}^{-1}$ )<sup>(24)</sup>. The values of  $k_1$  at different adsorption parameters were calculated from the plot of  $\log(q_e - q_t)$  as a function of the time for the best initial albumins concert ration at pH equal to 3,6 and temperature equal to 303k should give a linear relationship where the slope equal to  $(-k/2.303)$  and the intercept equal to  $\log q_e$ , is given by Figure-13.

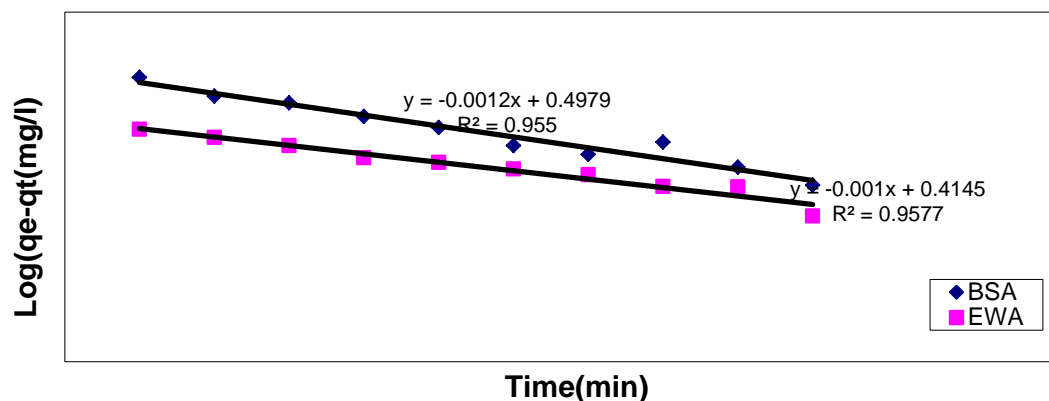


Fig-13: Lagergren equation for adsorption albumine on charcoal derived from almonds shell

The effect of temperature on albumins adsorption rate by almonds shell was examined further by applying the Arrhenius equation is:

$$K = Ae^{-E_a/RT}$$

Where  $k_1$  is the rate constant ( $\text{min}^{-1}$ ),  $A$  the pre. Exponent factor ( $\text{min}^{-1}$ ), which is a Measure of the accessibility of the reactive sites to the reactant,  $E_a$  is the Arrhenius activation energy ( $\text{KJ.mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J.mol}^{-1}.\text{k}^{-1}$ ) and  $T$  is the absolute temperature (k).

A plot of  $\ln k$  versus  $1/T$  yields a straight line, from which  $E_a$  and  $A$  can be obtained on the slope and intercept, respectively Fig-14.

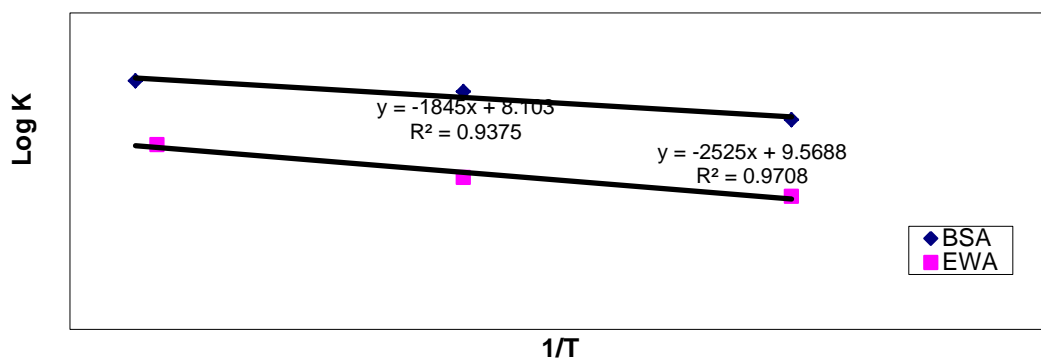


Fig-14: Relation between log K and 1/T

A more convenient form of the above equation is:

$$\text{Log K} = \log A - E_a/2.303RT$$

Table-2: Thermodynamic values and Active energy for albumin using charcoal derived at 303K

albumin	$\Delta H (\text{Kj.mol}^{-1})$	$\Delta G (\text{Kj.mol}^{-1})$	$\Delta S (\text{j.mol}^{-1}.\text{k}^{-1})$	$E_a (\text{j/mol}^{-1})$
BSA	-25.963	-5.582	67.26-	-48.346
EWA	-29.104	-7.021	-72.88	-35.326

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