RESEARCH ARTICLE

Adsorption of Albumin and Creatinine on Zinc Oxide (ZnO) Nanoparticles

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Received: 18th October, 19; Revised: 21th November, 19, Accepted: 15th December, 19; Available Online: 25th December, 2019

ABSTRACT

This study focused on the adsorption of albumin and creatinine on the surface of zinc oxide nanoparticles. Factors affecting adsorption, like contact time, adsorbent dose, concentration, temperature, PH, and shaking rate, were studied. The best conditions for adsorption were found at 298k, pH = (7), the concentration of (2.25, 0.5x10-3)g/dL, (30, 2.5)min, and weight of zinc oxide NPs (30, 10)mg for both albumin and creatinine respectively. We found that adsorption corresponds to Langmuir adsorption isotherms for albumin and Temkin adsorption isotherms for creatinin. Thermodynamic parameters were determined (average of ΔG = -12563.57(J/mol.K), ΔH = 25.740(kJ/mol), average of ΔS = 126.37(J/mol)) for albumin and (average of ΔG = -3348.45(J/mol.K), ΔH = 36.731(kJ/mol), average of ΔS = 132.22(J/mol)) for creatinine, Through the results of (ΔG), the system is spontaneous because of the negative values. Positive) ΔH (value clarify that process is endothermic. While ΔS value refers to the system is more random, the results also show that the adsorption type was physical, which means that it is multilayered. The type of bonding force between the molecules is Vander Waals force.

Keywords: Nanoparticles; Removal; Creatinine; and Albumin

International Journal of Pharmaceutical Quality Assurance (2019); DOI: 10.25258/ijpqa.10.4.23

How to cite this article: Kadhim, M.A., Salman, H.E., Ali, H.A. (2019). Adsorption of Albumin and Creatinine on ZnO Nanoparticles. International Journal of Pharmaceutical Quality Assurance 10(4): 689-695.

Source of support: Nil

Conflict of interest: None.

INTRODUCTION

Nanomaterials are deeming the building materials for (20th) century and its essential elements for biotechnology, nanotechnology, and communications technology, That is counted it the benchmarks for progress or civilization.[1] One of the unique features of nanomaterials is higher strength, enhanced dominance over the light spectrum, lighter weight, and also excellent chemical reactivity,[2] minimal size, high surface area, great stability, and multilateral chemistry.[3] Among the most widely used nanomaterials, zinc oxide has gained considerable attention in the scientific and medical communities, due to its important use in biomedical and antibacterial applications. This is due to their chemical and physical properties,[4] like high electrochemical binding coefficient, high chemical stability, zinc oxide is classified with a group (II-VI) as a semiconductor, between ionic and covalent semiconductors. Zinc oxide may be found in one dimensional 1D, two 2D, and three, 3D structures, and one-dimensional structures there are more than others.[5,6] ZnO shows (hexagonal symmetry) a wurzite structure or (cubic symmetry) rock salt structure, but ZnO crystals are more commonly stable with hexagonal symmetry as shown in Figure 1.[7]

There are several different ways for the preparation of ZnO nanostructures, including physical and chemical methods such as thermal evaporation, chemical vapor deposition (CVD), sol-gel deposition, electrochemical deposition, solvothermal and hydrothermal growth.[8-10] Recently, the interest in nanotechnology has increased because it has special characteristics that enable it to enter in several biological and medical applications.[11] Because of its proportional size to biological compounds e.g., proteins, DNA, cell membranes, and thus can interact in an advanced way at the cellular level (Figure 1).[12]

Organisms probably exposed to nanomaterials in different ways as in products with daily consumption such as cosmetics, foods, and also in the possible applications

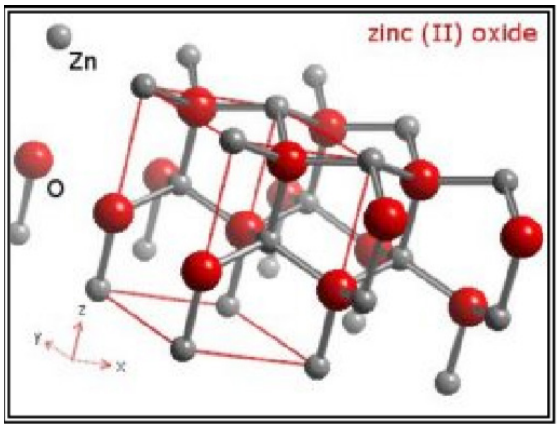

Figure 1: The crystal structure of zinc oxide.

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of it, in drug therapy, bioelectronics, and other uses.[13] The extent of biological compatibility and the risk of exposure to nanomaterials should be known. It is also important to recognize the molecular mechanisms of the interaction of the nanoparticle and biological systems. In the biological medium, many biomolecules can interact with nanomaterials, including proteins that may be absorbed on a nanoparticle that lead to formation nanoparticles-protein complexes, or so-called nanoparticles-protein corona, The adsorption of proteins by nanoparticles is done by a number of forces, including the hydrogen bonds, salvation forces, and Vander Waals interactions.[14] In this work, we studied the adsorption of two types of protein, such as Albumin and metabolic product of protein, such as Creatinine on the surface of zinc oxide nanoparticles.

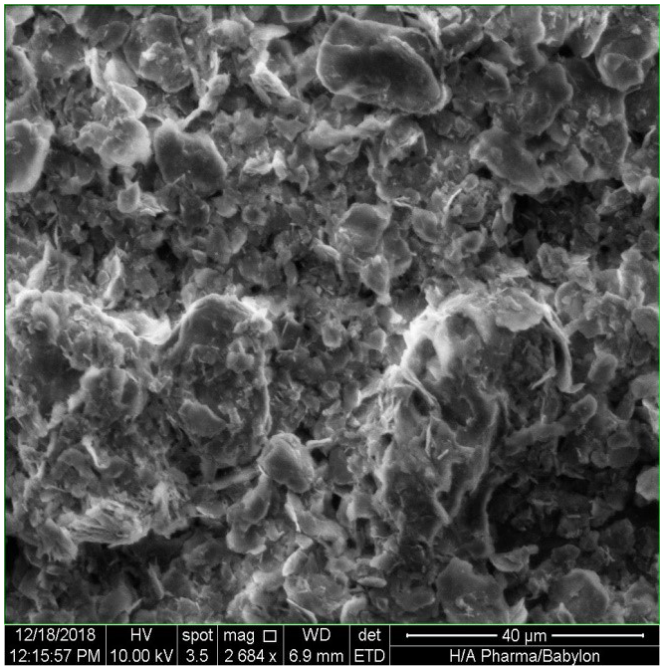

Figure 2: SEM characterization of zinc oxide NPs.

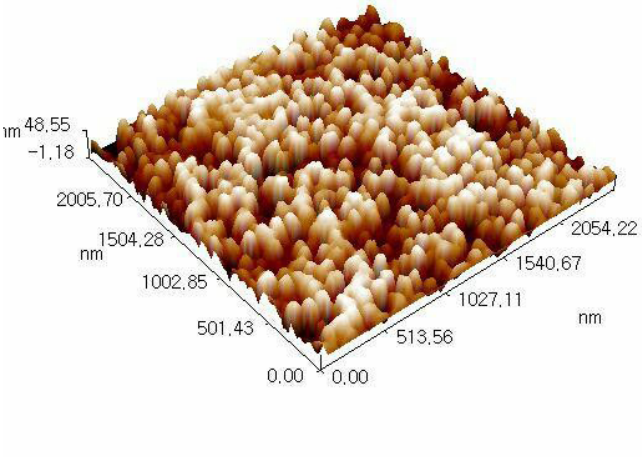

Figure 3: AFM characterization of zinc oxide NPs.

EXPERIMENTAL PART

Materials

All chemical materials used were obtained from various chemical suppliers, used without further purification, zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) from [Laboratory reagent Thomas baker, India.]. Sodium hydroxide (NaOH), ovalbumin, and creatinine from [BDH chemicals Ltd, Poole England]. Hydrochloric acid(HCl) from [SD Fine_Chemical limited-India].

Preparation of ZnO NPs

ZnO NPs was synthesized by adding a solution of (2M) NaOH to a solution of (0.5M) ZnSO4.7 H2O in droplets with continuous stirring until the (pH = 10). Then the precipitate was separated by a centrifuge and washed with deionized water three times with the return of the separation, and The resulting was dried at (70°C). Then zinc oxide NPs was characterized by using scanning electron microscopy (SEM), Atomic Force Microscopy, and X-Ray Diffraction Spectroscopy, as shown in Figures 2-4.

Figure 2 shows the form of zinc oxide under the Scanning Electron Microscopy that revealed a smooth particle morphology with high dense aggregation and shows the array of nanoparticles as arrange in several layers at a different size, varied shape. Figure 3 shows a three-dimensional image of a section of the surface of nanomaterials showing the rise of molecular clusters that are about 48.55nm and that the average particle size is about 73.97nm. Figure 4 shows the XRD pattern of ZnO NPs, strong diffraction peaks appeared at 31.78°, 34.33°, and 36.17°, which correspond to 100, 002 and 101 planes respectively were shown hexagonal wurtzite structure of ZnO,[15,16] the Crystallite size of ZnO NPs was calculated by Debye-Scherrer's equation[16,17] to be 33.1 nm.

Adsorption Experiments.

Adsorption of albumin and creatinine on ZnO NPs were studied. By mixing (40mg) of ZnO NPs with (100µL) of (2.25g/dL) albumin solution and ($0.5x10^{-3}$g/dL) of creatinine solution and completed the solution to 1000µL with distilled water, these were placed in the thermostated shaker at (140rpm)

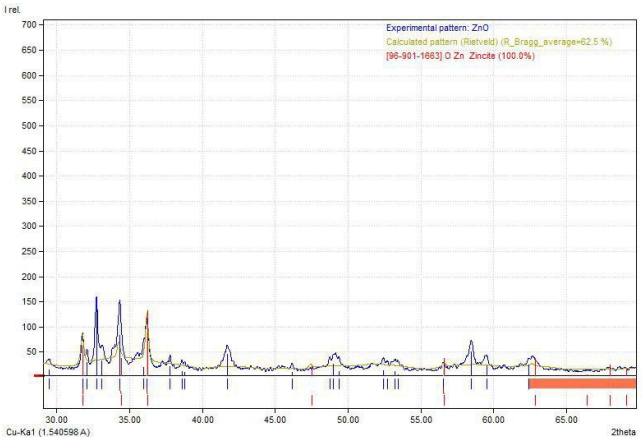

Figure 4: XRD characterization of zinc oxide NPs.

for different times, after that separated happened by using a centrifuge for (20min) twice. Different parameters were studied, including the time of mixing the solutions. Also, five different weights of ZnO were taken to know the effect of the weight of the adsorbent material; the effect of albumin and creatinine concentration also studied by taking five different concentrations. Temperature effect was also studied by four different temperatures (298 – 318K), pH effect was studied by setting the pH of the adsorptive solution by (0.5 M) of HCl or (0.5 M) of NaOH, the effect of mixing velocity on adsorption finally determined by using five different speeds (40–280 rpm). The concentration of albumin and creatinine was calculated by using a commercial kit (Cromatest, Linear Chemicals-Spain) through an optical method by Spectrophotometer (Shimadzu UV-Vis 1800- Japan). The amount of albumin and creatinine adsorbed on ZnO NPs adsorbent calculated through this equation.[18]

$$Qe = \frac{(Co - Ce)\ V}{m} \quad (1)$$

Where Qe refers to (adsorbent capacity) (mg/g) the amount of substance adsorbed at equilibrium, Ce and Co ($mg.L^{-1}$) are the concentrations of substance adsorbed at equilibrium and initial respectively, V is the volume of the substance adsorbed solution (L), and m is refers to adsorbent mass (g). The percentage of adsorption may exist through this equation:

$$\%\ \text{Adsorption} = \frac{(Co - Ce)}{m} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Effect of Contact Time

The experiments of contact time of Albumin and Creatinine were conducted to know its effect on adsorption, as shown in Figure 5. The time of equilibrium was reached within (30 min and 2.5 min) for Albumin and Creatinine, respectively.

Effect of Adsorbent Dose

Effect of ZnO NPs weight is studied by changing the dose of ZnO NPs (10-50 mg) while keeping the first concentration 2.25 g/dL and $0.5x10^{-3}$ g/dL and contact time 30min and 2.5min for Albumin and Creatinine respectively, as we see in Figure 6. The percent of adsorption of albumin increased with increasing the dose of ZnO NPs, that because of the existence of bigger surface area with more active functional groups,[19] and then reached a state of equilibrium, as an outcome of the saturation of the sites active in protein. The percent of the adsorption of creatinine reached a state of equilibrium Since the start of the interaction as a result of the saturation of sites active in the metabolic product of protein.

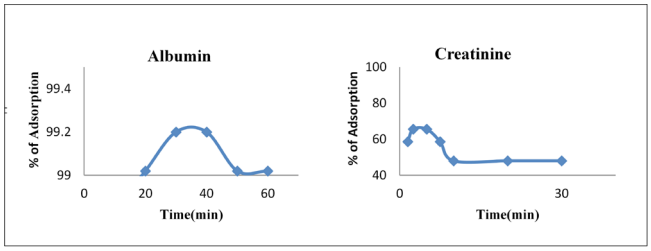

Figure 5: Effect of contact time on percentage adsorption of albumin and creatinine on ZnO NPs.

Effect of pH

Adsorption experiments have been done at pH (2-11) at optimum conditions for this study. As elucidated in Figure 7, albumin adsorption decreases by increasing the pH value from (2–7) because it is an acidic protein. And because of the basal nature of creatinine, the adsorption increased by increasing the pH value. Then, after pH = 7, there was no remarkable change. SO, pH=7 was selected for subsequent experiments.

The effect of temperature

Different temperatures have been applied (298-318K). The results that were existing in Figure 8 showed that the amount of adsorption increases with temperature increase due to the increased kinetic energy of molecules helps to enter the pores on the surface of zinc oxide NPs.[20] The temperature of 25°C was chosen for the rest of the experiments, so due to the breakdown of proteins at high temperatures.

Effect of concentration

By using five different concentrations of albumin and creatinine at 298k and pH = 7. The results clear in Figure 9 showed

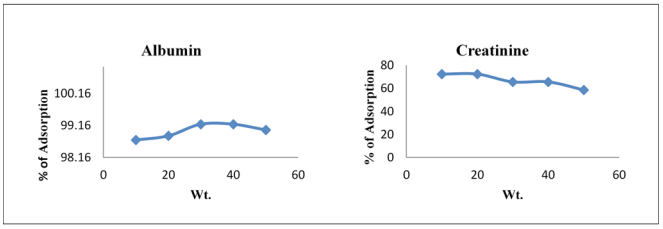

Figure 6: Effect of ZnO NPs weight on percentage adsorption of albumin and creatinine.

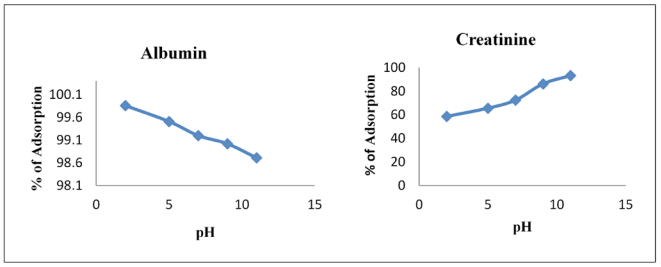

Figure 7: Effect of pH on the percentage adsorption of albumin and creatinine on ZnO NPs.

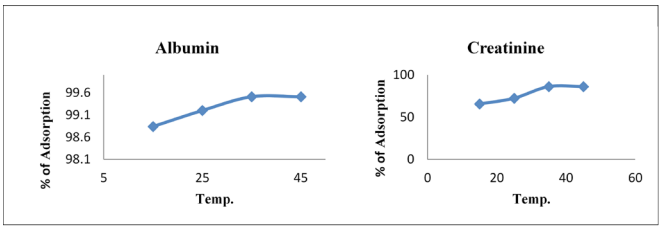

Figure 8: Effect of temperature on percentage adsorption of albumin and creatinine on ZnO NPs.

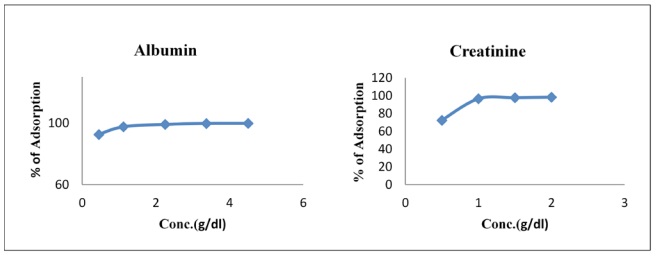

Figure 9: Effect of concentration of albumin and creatinine on percentage adsorption.

that the amount of adsorption increases with increasing concentration, this is due to the increase in the active groups which are associated with the active sites on the surface of zinc oxide NPs by increasing the concentration leading to increased adsorption.

Effect of shaking rate:

Figure 10 clarify the effect of different shaking speeds on the adsorption for five different speed, we showed that adsorption increases with increasing shaking rate until it reaches a state of equilibrium that due to increasing kinetic energy this speeds up the link with effective sites on ZnO NPs.

Table 1 shows the best adsorption ratios for both albumin and creatinine during the various experiments mentioned above; we showed that the percentage for adsorption of albumin on the surface of ZnO NPs was higher than creatinine by 28%, This may be due to the large molecular structure of albumin and high molecular weight as well as high surface area compared to creatinine.

Adsorption Isotherm

Adsorption isotherms represent one of the most important data to clarify the mechanism of adsorption. Table 2 shows the quantities of adsorbed albumin and creatinine on ZnO NPs (Qe) and equilibrium concentration (Ce).

The number of equilibrium data are usually extracted by using adsorption isotherms.

Table 1: Comparison study of adsorption ratio of albumin and creatinine.

	% adsorption of albumin	*% adsorption of creatinine*
Effect of contact time	99.2	65.6
Effect of adsorbent dos	99.2	72.4
Effect of pH	99.2	72.4
Effect of temperature	99.2	72.4
Effect of concentration	99.2	72.4
Effect of shaking rate	99.2	72.4
Rate of adsorption ratio	99.2	71.2

3.7.1 Langmuir Isotherm

This isotherm is explained by this equation:

$$\frac{Ce}{Qe} = \frac{1}{a\,b} + \frac{Ce}{a} \qquad (3)$$

where : Qe (mg/g) is the amount of adsorbed at equilibrium, Ce (mg/L) represents the equilibrium concentration, (a,b) are Langmuir constants, that represent the energy of adsorption and adsorption capacity respectively.[21,22]

From this drawing, we get Langmuir constants (a and b) and the value of the coefficient of application(R^2), which shows how well the adsorption is compatible with this isotherm.

3.7.2 Freundlich Isotherm

It applied to adsorption on heterogeneous surfaces; it also describes multilayer adsorption.[23] This equation represents it:

$$Log\ Qe = Log\ K_f + 1/n\ Log\ Ce \qquad (4)$$

Where Ce (mg/L) represent the equilibrium concentration, Qe (mg/g) represent the amount of metal adsorbed at equilibrium , and Freundlich constants that (K_f) adsorption capacity and (1/n) adsorption intensity.[24,25]

From this drawing, we get the value of the coefficient of application(R^2) and Freundlich constants (Kf),(1/n), that (n) indicates the intensity of adsorption, the greater the value of (n), the more favorable it is in adsorption.

3.7.3 Temkin Isotherm

The following equation represents this isotherm:

$$Qe = B\ ln\ AT + B\ ln\ Ce \qquad (5)$$

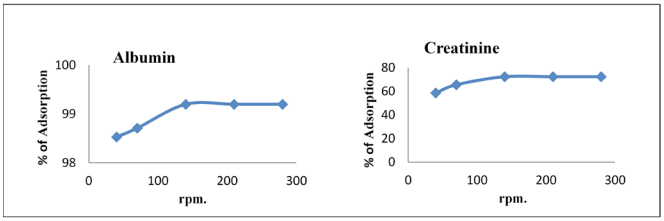

Figure 10: Effect of shaking rate on percentage adsorption of albumin and creatinine on ZnO NPs.

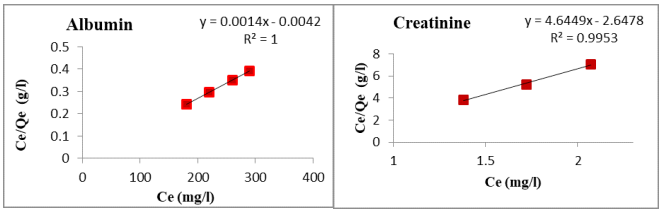

Figure 11: Plot of Langmuir isotherm for Albumin and Creatinine.

Table 2: Adsorption values of Albumin and Creatinine on ZnO NPs at (298K).

	Albumin			*Creatinine*		
Wt. of ZnO g	*Ce mg/L*	*Qe mg/g*	*Ce/Qe g/l*	*Ce mg/L*	*Qe mg/g*	*Ce/Qe g/L*
0.01	290	740.3	0.391	1.38	0.362	3.812
0.02	260	741.3	0.350	1.38	0.362	3.812
0.03	180	744	0.241	1.72	0.328	5.243
0.04	180	744	0.241	1.72	0.328	5.243
0.05	220	742.6	0.296	2.07	0.293	7.064

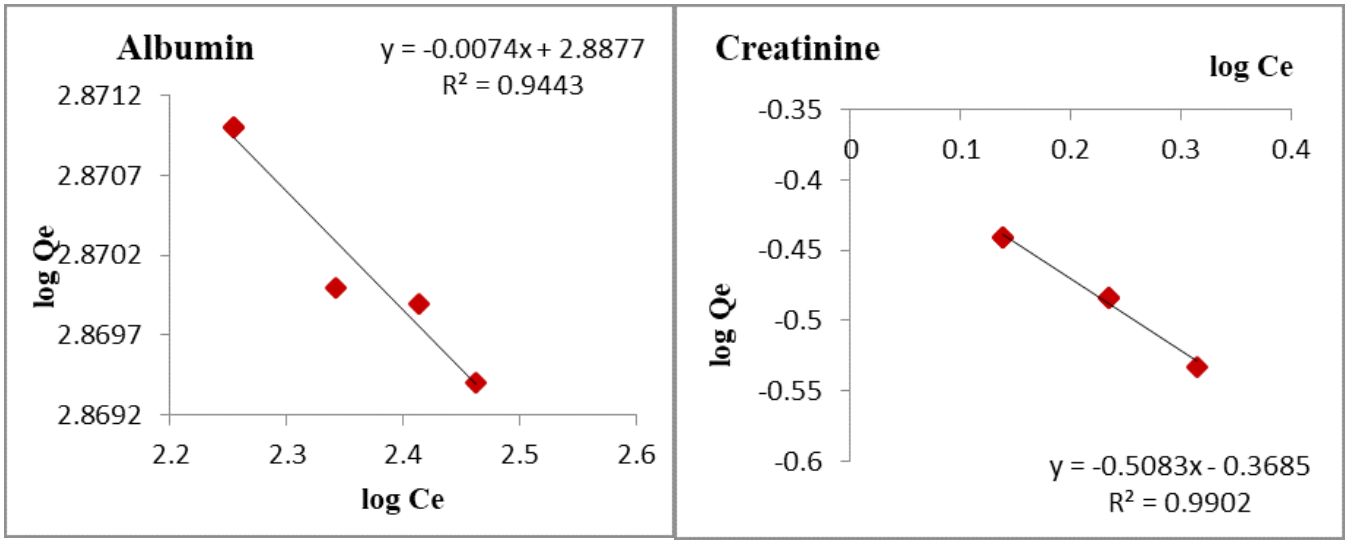

Figure 12: Plot of Freundlich isotherm for Albumin and Creatinine.

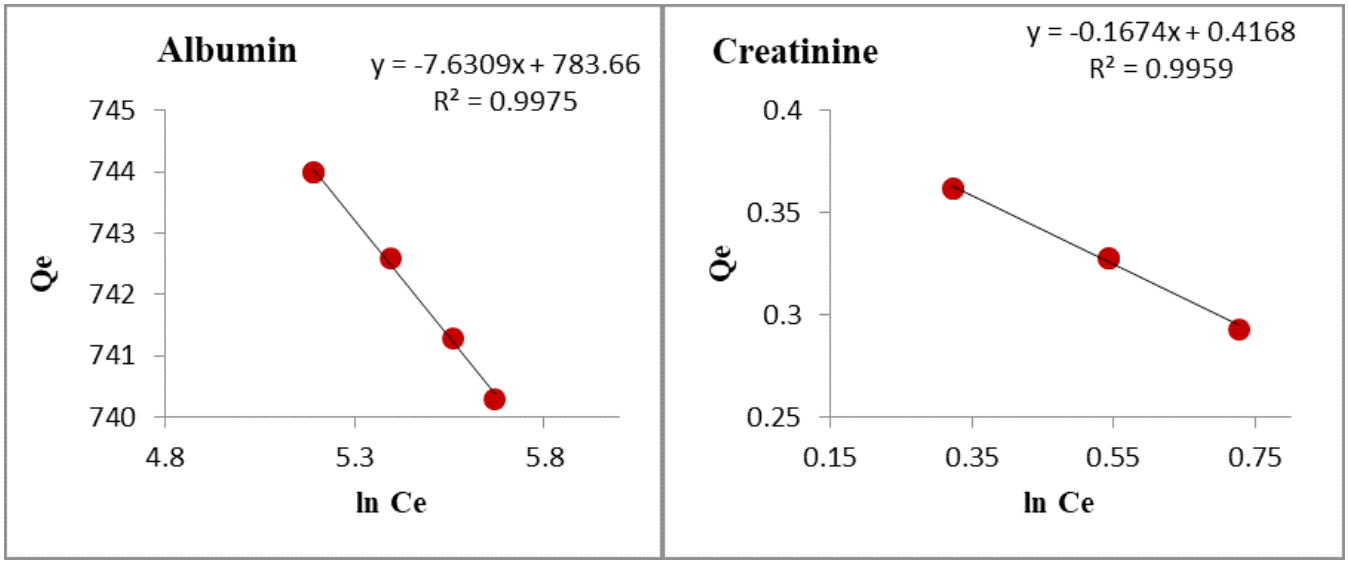

Figure 13: Plot of Temkin isotherm for Albumin and Creatinine.

AT represent equilibrium binding constant, (B) is related to the heat of adsorption.[21]

From this drawing, we get Temkin constant (A_T),(B), and also the value of the coefficient of application (R^2).

By drawing linear equations of isothermets Langmuir, Freundlich and Temkin for adsorption of albumin and creatinine, the constants of each isotherm were extracted as shown in Table 3 in addition to the coefficients of applicability (R^2).

Thermodynamic parameters

In this work, thermodynamic parameters were calculated in Table 4 and Figure 14.

Thermodynamic parameters: (ΔG), (ΔH) and (ΔS) were found by applying this equations.[26]:

$$\Delta G = - RT \ ln Keq \quad (6)$$

$$Keq = \frac{Qe\ m}{Ce\ v} \quad (7)$$

$$lnKeq = - \quad + Constant \quad (8)$$

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

Thermodynamic function ΔG, ΔH, and ΔS of Albumin and Creatinine on the adsorbent surface that shows in Table (4), the process was spontaneous through the negative values of ΔG, Positive (ΔS) values show that the system is more random, while the positive (ΔH) value clarified that the process is endothermic.

CONCLUSION

In the present work various parameters were studied on the adsorption process and The results showed the best conditions for effected on adsorption of albumin and creatinine on ZnO NPs at 298k, pH = 7, concentration of (2.25, 0.5x10-3) g/dl, (30, 2.5)min and weight of ZnO NPs (30, 10)mg for both albumin and creatinine respectively. The results of isotherm studies showed Langmuir, Freundlich and Temkin isotherms. Langmuir model was more compatible for describing adsorption of albumin, while Temkin model was

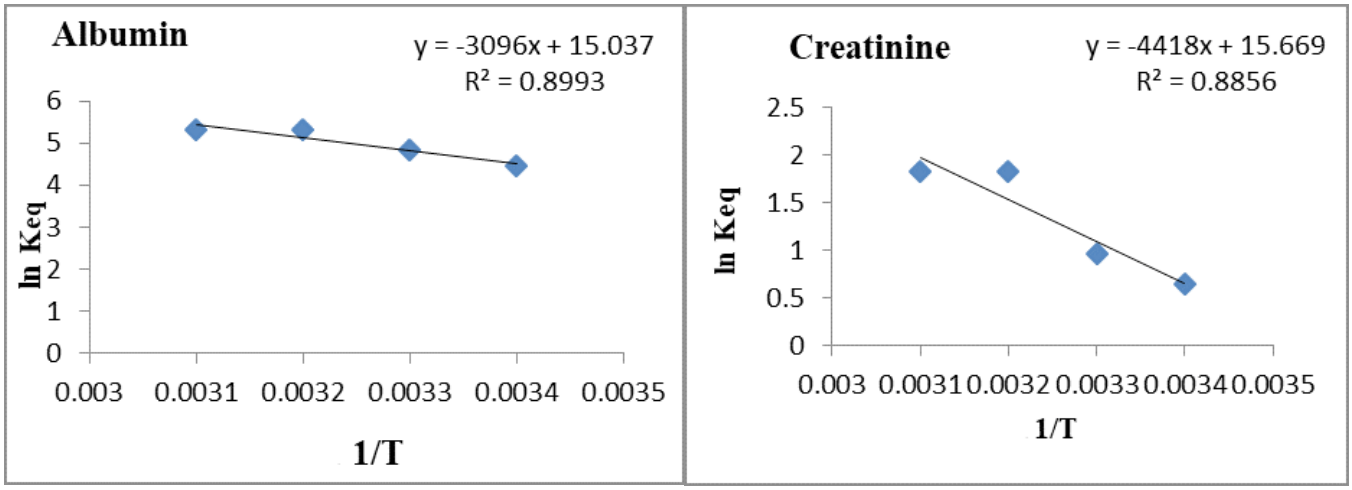

Figure 14: The relationship between ln Keq and 1/T for adsorption of Albumin and Creatinine to calculate a value of ΔH.

Table 3: The constants of adsorption isotherms at (298K).

	Langmuir			*Freundlich*			*Temkin*		
Adsorbate	*a*	*b*	R^2	*1/n*	K_f	R^2	*B*	A_T	R^2
Albumin	714.2	-0.333	1	-0.0074	772.1	0.9443	-7.6309	2.511×10^{-45}	0.9975
Creatinine	0.215	-1.756	0.9953	-0.5083	0.428	0.9902	-0.1674	0.0829	0.9959

Table 4: Thermodynamic function ΔG, ΔH and ΔS of Albumin and Creatinine on ZnO NPs at (288-318)K.

	Albumin			*Creatinine*		
T(k)	*ΔG(J/mol.K)*	*ΔH(J/mol)*	*ΔS(J/mol)*	*ΔG(J/mol.K)*	*ΔH(J/mol)*	*ΔS(J/mol)*
288	-10650.4	25740.1	126.3	-1534.8	36731.2	132.8
298	-11941.8		126.4	-2366.0		131.1
308	-13610.1		127.7	-4670.7		134.4
318	-14052.0		125.1	-4822.3		130.6

more compatible for describing adsorption of creatinine. Thermodynamic parameters explained that the adsorption of albumin and creatinine by ZnO NPs is spontaneous. The system is more random and endothermic, the results also show that the adsorption type was physical, which means that it is multilayered and the type of bonding forces between the molecules is Vander Waals force.

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