

Dependence of Equilibrium, Kinetics and Thermodynamics of Zn (II) Ions Sorption from Water on Particle Size of Natural Hydroxyapatite Extracted from Bone Ash

Reza Bazargan-Lari, Mohammad Ebrahim Bahrololoom and Afshin Nemati

Abstract—Heavy metals have bad effects on environment and soils and it can uptake by natural HAP. Natural Hap is an inexpensive material that uptake large amounts of various heavy metals like Zn (II). Natural HAP (N-HAP), extracted from bovine cortical bone ash, is a good choice for substitution of commercial HAP. Several experiments were done to investigate the sorption capacity of Zn (II) to N-HAP in various particles sizes, temperatures, initial concentrations, pH and reaction times. In this study, the sorption of Zinc ions from a Zn solution onto HAP particles with sizes of 1537.6 nm and 47.6 nm at three initial pH values of 4.50, 6.00 and 7.50 was studied. The results showed that better performance was obtained through a 47.6 nm particle size and higher pH values. The experimental data were analyzed using Langmuir, Freundlich, and Arrhenius equations for equilibrium, kinetic and thermodynamic studies. The analysis showed a maximum adsorption capacity of N-HAP as being 1.562 mmol/g at a pH of 7.5 and small particle size. Kinetically, the prepared N-HAP is a feasible sorbent that retains Zn (II) ions through a favorable and spontaneous sorption process.

Keywords—Natural Hydroxyapatite, Heavy metal ions, Adsorption, Zn removal, kinetic model, bone ash

I. INTRODUCTION

HEAVERY metal ions flow into water from industrial activities such as electroplating industries, electronic equipment manufacturing, mining, and chemical processing plants. In addition, due to their non-biodegradability and toxic nature, they should be treated entering wastewater or better yet, separated from wastewater. Organic pollutants and heavy metals limit agricultural application of sewage sludge, however, as they tend to accumulate along the food chain and bring potential risks to animals and humans [1]. The recommendation of the World Health Organization for the safe amount of Zn (II) is 5 mg/L in drinking water [2]. The metal has also been reported to bio-accumulate into fauna and flora, creating serious ecological problems at higher concentrations.

R. Bazargan-Lari. Author is with the Department of Mechanical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran.(rbazarganlari@gmail.com)

M. E. Bahrololoom Author is with Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, 7134851154, Iran.

A. Nemati Author is with the Department of Mechanical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran

There are various methods for the removal of heavy metals such as chemical precipitation, reverse osmosis, ion exchange, coagulation, and adsorption [2]. From these methods, adsorption is the most common due to its high uptake and the lower cost. At present, there is growing interest in using low cost, non-conventional alternative materials which are considered to be waste such as grape stalks, crop millinwaste, and sawdust, instead of traditional adsorbent for heavy metals removal from wastewater [3]. Natural Hydroxyapatite obtained from bovine cortical bone ash is a stable and inexpensive material that can be produced through a simple method. Hydroxyapatite has a good ability to remove inorganic cations, which has led to the development of its use in removing heavy metals from contaminated water [4]. Hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ is a unique inorganic compound because of its high removal capacity for divalent heavy metal ions, and synthetic HA has been used to remove heavy metals such as Pb, Zn, Cu, Cd, Co, and Sb from water [5], [6], [7] and [8]. The possible reaction mechanisms for metal immobilization include: (a) ion exchange processes [8], [9] and [10]; (b) surface complexation [11], [12]; (c) dissolution of HA and precipitation of new metal phosphates [13] and [14], and (d) substitution of Ca in HA by other metals during re-crystallization (co-precipitation) [9] and [15]. However, because of the limited knowledge regarding the relative contribution of each process in removing metals, it seems that the above four mechanisms could all be involved [9]. Wastewater from surface finishing and the plating industry usually contain metal-ion concentrations much higher than permissible levels. Due to their high toxicity, industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in to the environment. Various techniques have been employed for the treatment of heavy metals including precipitation, adsorption, ion-exchange and reverse osmosis, which are usually expensive techniques. In the present research, we attempted to remove Zn (II) ions from wastewater by using natural hydroxyapatite particles obtained from bone ash. This technique is surely more economical than the above mentioned techniques. This paper works on the amount of Zn ions that uptake by natural HAP particles in different sizes by Langmuir and Freundlich isotherm equations for equilibrium, and investigates the kinetic and thermodynamic by the pseudo first and second

order models and Arrhenius equations in this sorption process.

II. MATERIALS AND METHODS

A. Materials and instruments

Bovine femur, tibia, humerus and ulna were chosen as the main starting biological material. Spongy bones were discarded and the cortical bone de-fleshed. The bone marrow and all pieces of meat and fat were removed. By using a gas torch and applying direct flame to the cleaned bone, the organic components were burned. The product of this thermal process contained some char due to the burning of the organic components. To remove the remaining char, the black powder (bone ash) was placed in an air furnace at different temperatures between 600 °C to 1100 °C for 3 hours, and then was finally left to cool inside the furnace. Following this process, the black ash turned into a white granular powder[16].

All the materials and aqueous solutions were prepared using double distilled water and the Zn solution was prepared from Zn(NO₃)₂•6H₂O diluted in deionized water. A Multiline 330i pH-meter was used to determine pH. Various buffer solutions of different pH values (4.50, 6.00, and 7.50) were used in these experiments. 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the initial pH of the solution. To determine the amount of Zn in the solution, an AA-680 atomic absorption /flame emission spectrophotometer made by Shimadzu Company was used.

B. Sorption Experiments

To determine the amount of Zn (II) sorbed on N-HAP the following equation can be used:

$$q_e = (C_0 - C_e) \times v/m \quad (1)$$

Where C₀ is the initial concentration of metal ion (mmol/L) and C_e is the concentration of metal ions after equilibrium. V and m are volume solution (L) and mass of adsorbent (g), respectively, whereas q_e is the adsorption capacity per unit mass of N-HAP (mmol/g);

1. Equilibrium Isotherm

There are several models that express a relation between the amounts of sorption and the residual solute concentration. The most frequent models are the Langmuir and Freundlich adsorption isotherm models:

Langmuir is the most important model of monolayer adsorption, based on the assumption that there are a fixed number of adsorption sites, and each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness). All sites are equivalent and there is no interaction between the adsorbed molecules [3].

0.2 g of N-HAP was added to 200mL of Zn ion solution with three different pH values and initial concentrations ranging from 0.1 to 1.2 mmol/L for two different particle sizes of 1537.6 nm and 47.6 nm, in order to determine the effect of the particle sizes and the pH. The solution was poured in a flask and shaken in an incubator with a speed of 300 rpm at a temperature of 25°C .After 24 hours, the adsorbent was separated from the solution with a 0.45µm membrane and the

solution was analyzed using an atomic absorption spectrophotometer to determine the equilibrium concentration of Zn (II) ion.

The Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{1}{q_m} C_e \quad (2)$$

Where q_m is the maximum adsorption capacity (mmol/g) and b is the Langmuir isotherm constants, according to Langmuir equation.

The degree of suitability was estimated from the value of separation factor, which can be obtained by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

The values less than unity show that the sorption of metal ions to N-HAP particles is optimum and the sorption process is favorable. Table I shows the optimum range of R_L.

TABLE I
RANGES OF R_L

Values of R _L	Type of isotherm
R _L > 1	Unfavorable
R _L = 1	Linear
0 < R _L < 1	Favorable
R _L < 0	Irreversible

The Freundlich isotherm model is an experimental model, usually expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Or can be expressed in a logarithmic form as:

$$\ln q_e = b_F \ln C_e + \ln K_F \quad (5)$$

Where K_F is the Freundlich constant and b_F is the Freundlich exponent.

2. Sorption Kinetics

0.2 g of N-HAP was added to 200mL of Zn solution with three different pH values and was then poured in to a flask and placed in a shaking incubator at a speed of 300 rpm to measure the adsorption of N-HAP in various times of 5, 10, 15, 30, 60,120, 240, 480,720 and 960 minutes.

The distribution ratio (K_d) and removal efficiency (E) of the adsorbent on the Zn (II) ions were measured as follows:

$$K_d = \frac{\text{amount of Zn in adsorbent}}{\text{amount of Zn in solution}} \times v/m \quad (6)$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (7)$$

Where C₀ and C_e are the initial and final equilibrium concentrations (mmol/g), v is the volume of the solution (mL) and m is the weight of the adsorbent (g). This equation can be expressed as follows:

$$\text{removal efficiency (\%)} = \frac{100K_d}{K_d + \frac{v}{m}} \quad (8)$$

The two main types of sorption kinetic models, namely reaction-based and diffusion-based models, were adopted to fit

the experimental data. The study of sorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid/solution interface [17]. In this paper, the research is on reaction based models that contain pseudo first and second order models.

To investigate the reaction-based model, pseudo-first-order and pseudo-second-order models were employed. The pseudo first-order model and pseudo second-order model can be expressed by Eqs. (8) and (9), respectively:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{9}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

Solving equation 9 and 10 for the initial and boundary conditions of $t=0$ to $t=t$ and $Q_t=0$ to $Q_t=Q_0$, the following equations can be obtained:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{11}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

3. Adsorption Thermodynamic Studies

Standard enthalpy change (ΔH°), standard free energy change (ΔG°) and standard entropy change (ΔS°) are thermodynamic parameters that can be obtained by the following equations:

$$K_e = \frac{q_e}{C_e} \tag{13}$$

$$\Delta G^\circ = -RT \ln K_e \tag{14}$$

$$\ln K_e = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{15}$$

Thermodynamic experiments were carried out at a temperature range of 15°C to 55°C and in these equations, the temperature unit is (K).

Another important equation in thermodynamic investigations is the Arrhenius equation. A modified Arrhenius-type equation related to the surface coverage (θ) is sticking probability, S^* . This is a function of the adsorbate/adsorbent system, which is a measure of the potential of an adsorbate to remain on the adsorbent indefinitely. The Arrhenius equation can be expressed as [18]:

$$S^* = (1 - \theta) \exp - \left(\frac{E_a}{RT} \right) \tag{16}$$

Where θ is surface coverage:

$$\theta = 1 - \frac{C_e}{C_0} \tag{17}$$

Where E_a is activation energy and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

III. RESULTS AND DISCUSSION

A. Equilibrium Studies

Values of q_{max} and b were determined from the linear plot of C_e/q_e versus C_e that were listed with the correlation coefficients (R^2) in Table 2, and with the linear plot of $\ln q_e$ versus $\ln C_e$. By using Freundlich isotherm model, the values of bF and KF were obtained and shown in Table III. In the

initial concentrations of the Zn ion solution that was between 0.1 to 1.2 mmol/L, the sorption data showed a good fit with the Freundlich isotherm model and it had a better fit than the Langmuir isotherm model ($R^2 = 0.99$). Figures 1 and 2 were plotted for the Langmuir isotherm model and Figs. 3 and 4 were for the Freundlich isotherm model for sorption of Zn (II) ions onto N-HAP in different particle sizes and pH values. The maximum capacity of sorption (q_{max}) and the constant for the two models that were listed in Table 2 showed better sorption for Zn (II) ions in higher pH values and the 47.6 nm size. The maximum capacity of sorption was 1.562 mmol/g for pH=7.50. Application of the Freundlich model to the equilibrium data of Zn(II) ion indicates the monolayer coverage of N-HAP by the Zn(II) ion, but this was to non-distinct or multiple sites of adsorption, unlike the Langmuir model, which is to distinct localized adsorption sites.

Table IV shows the values of R_L for the initial concentration of 0.1 mmol/L and different pH values that show favorable isotherm sorption with respect to Table I and the following table.

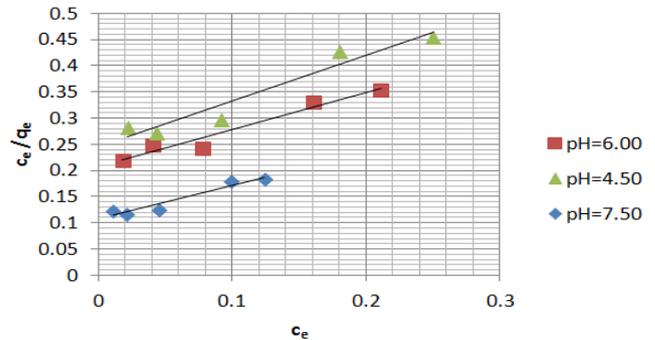


Fig. 1 Langmuir isotherm model for 47.6 nm size natural HAP particles

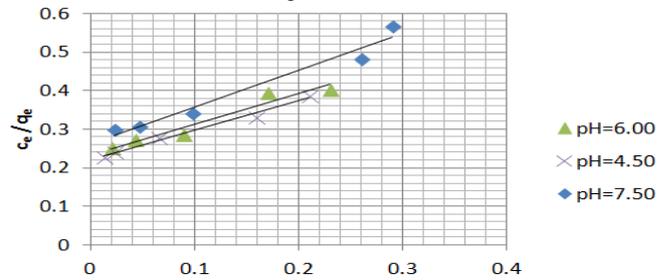


Fig. 2 Langmuir isotherm model for 1537.6 nm size natural HAP particles

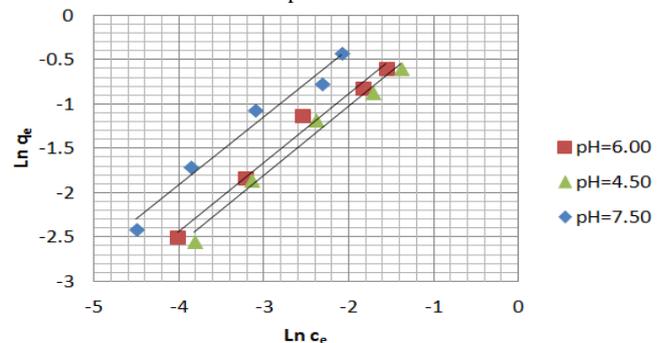


Fig. 3 Freundlich isotherm model for 47.6 nm size natural HAP particles

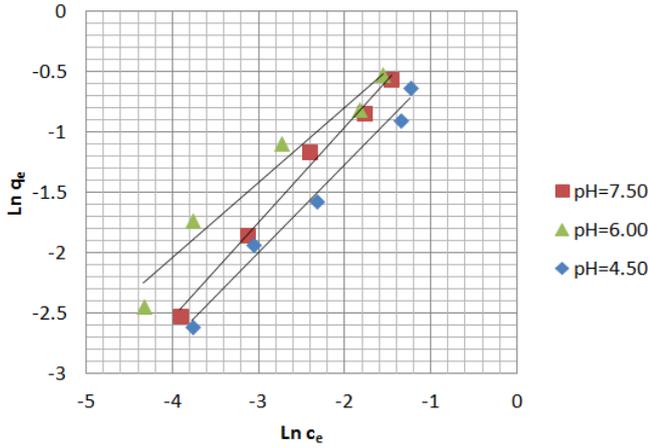


Fig. 4 Freundlich isotherm model for 1537.6 nm size natural HAP particles

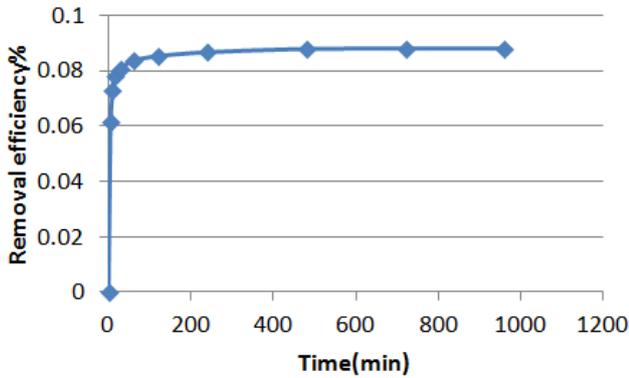


Fig. 5 Removal efficiency of N-HAP

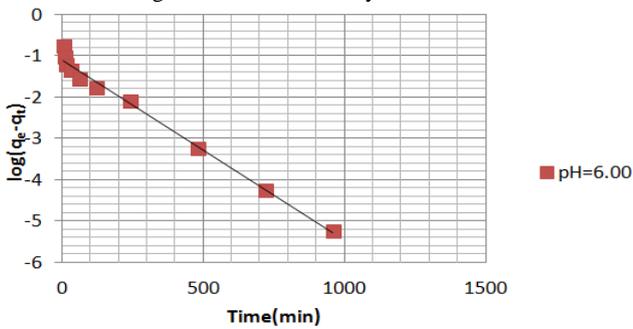


Fig. 6 Pseudo-first order rate constants for adsorption of the zinc ion onto natural HAP

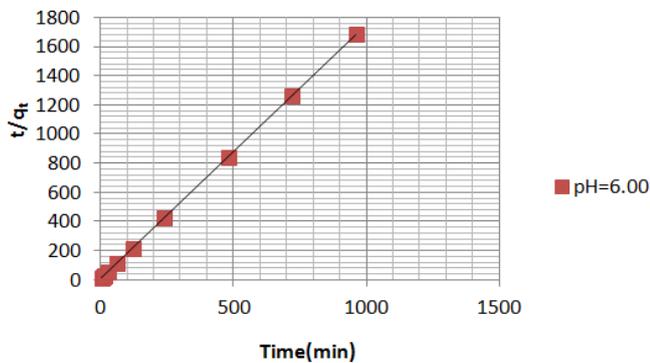


Fig. 7 Pseudo-second order rate constants for adsorption of zinc ion onto natural HAP

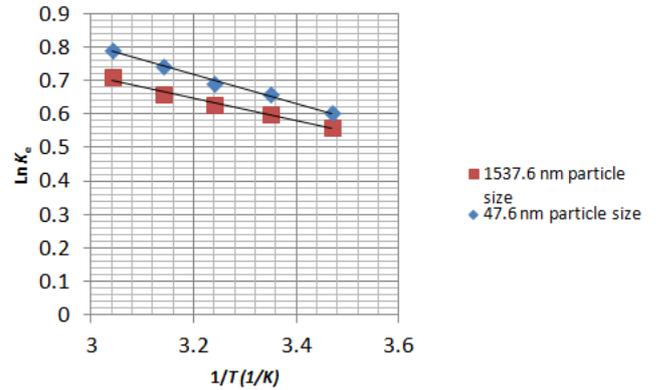


Fig. 8 The plots of $\ln K_e$ versus $1/T$ for the adsorption of the Zn (II) ion on natural HAP for both 1537.6 nm and 47.6 nm particle size

TABLE II
THE LANGMUIR CONSTANTS FOR ADSORPTION OF ZINC IONS ONTO NATURAL HAP

	q_{max} (mmol/g)	b (L/g)	R^2
1537.6 nm size N-HAP			
pH=4.50	1.051	3.610	0.963
pH=6.00	1.114	4.007	0.972
pH=7.50	1.310	3.454	0.982
47.6 nm size N-HAP			
pH=4.50	1.184	3.433	0.949
pH=6.00	1.410	3.426	0.969
pH=7.50	1.562	5.983	0.986

TABLE III
FREUNDLICH ISOTHERM CONSTANTS FOR ADSORPTION OF ZINC IONS ONTO NATURAL HAP

	K_F (mmol/g)	b_F (L/g)	R^2
1537.6 nm size N-HAP			
pH=4.50	0.725	1.185	0.985
pH=6.00	0.79	1.579	0.993
pH=7.50	0.624	1.857	0.996
47.6 nm size N-HAP			
pH=4.50	0.782	1.713	0.989
pH=6.00	0.77	1.861	0.991
pH=7.50	0.761	2.954	0.995

TABLE IV
 R_L FOR INITIAL CONCENTRATION OF 0.1 MMOL/L

	R_L
1537.6 nm size	
pH=4.50	0.743
pH=6.00	0.713
pH=7.50	0.733
47.6 nm size	
pH=4.50	0.744
pH=6.00	0.753
pH=7.50	0.625

TABLE V
PSEUDO-FIRST AND SECOND ORDER RATE CONSTANTS FOR ADSORPTION OF ZINC IONS ONTO NATURAL HAP

Sorberent	Pseudo-first-order rate constants		Pseudo-second-order rate constants	
	$K_1(1/\text{min})$	R^2	$K_2(\text{g}/\text{mmol}\cdot\text{min})$	R^2
Natural HAP	0.004	0.989	0.803	0.999

TABLE VI
THERMODYNAMIC PARAMETERS OF ZINC SORPTION ON NATURAL HAP (ΔH° & ΔS°)

	$\Delta H^\circ (\text{KJ}\cdot\text{mol}^{-1})$	$\Delta S^\circ (\text{KJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	R^2
1537.6 nm size N-HAP	6.370	32.83	0.977
47.6 nm size N-HAP	8.194	39.96	0.993

TABLE VII
THERMODYNAMIC PARAMETERS OF ZINC ION SORPTION ON NATURAL HAP (ΔG°)

	K_s	$-\Delta G^\circ (\text{KJ}\cdot\text{mol}^{-1})$
1537.6 nm size N-HAP	6.370	32.83
47.6 nm size N-HAP	8.194	39.96

TABLE VIII
THERMODYNAMIC PARAMETERS OF THE ZINC ION SORPTION ON NATURAL HAP (S^* & E_a)

	S^*	$E_a (\text{KJ}\cdot\text{mol}^{-1})$
1537.6 nm size N-HAP	0.0232	5.304
47.6 nm size N-HAP	0.0139	6.368

B. Kinetic Studies

The maximum efficiency of N-HAP in sorption of the Zn (II) ion obtained at pH=7.50 and for the 47.6 nm particle size was about 88% (Fig. 5). The results show lower adsorption in comparison to recent researches which were carried out by commercial HAP.

The difference in adsorption results may have two reasons:

- 1) Using N-HAP instead of commercial HAP.
- 2) The difference between the dosage of N-HAP used in these experiments and that of previous researches.

With the plot $\log(q_e - q_t)$ versus time, the values of k_1 can be determined. The slopes and intercepts of plots t/q_t versus t were used to calculate the second-order rate constants k_2 and q_e . As can be seen from Figs. 6 and 7, the results obtained for the adsorption of Zn (II) ion onto N-HAP were fitted to Eqs. (11) and (12), and an approximate linear fit was observed.

The values of k_1 , k_2 and R^2 , shown in Table 5, clearly indicate the pseudo second-order model provided better correlation

coefficients than the pseudo first-order model for adsorption of zinc ions onto N-HAP, which suggests that this adsorption system is not a first-order kinetic adsorption process.

Therefore, the zinc ion adsorption onto the N-HAP belongs to the second-order kinetic model and the adsorption is a chemical process.

C. Thermodynamic Studies

Plotting $\ln K_0$ versus $1/T$ gives a straight line with a slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° , ΔS° and ΔG° were calculated from Fig. 8 and reported in Tables 6 and 7.

The negative values of ΔG° confirm the feasibility and the spontaneous nature of the zinc ion sorption. The value of ΔH° was positive, indicating that the sorption reaction was endothermic. The positive value of ΔS° during the zinc ion sorption indicates that there was an increase in the randomness in the solid/solution interface during the adsorption process.

The plot of $\ln(1-\theta)$ versus $1/T$ will give a linear plot with an intercept of $\ln S^*$ and a slope of E_a/R (Fig. 9) as shown in Table (8). The value of S^* was found to be 0.1, which is very close to zero, indicating that the adsorption follows Shemisorptions [19].

IV. CONCLUSIONS

In this study, sorption experiments of the Zn (II) ion onto N-HAP, extracted from bovine ash, were used for the removal of this metal ion from aqueous solutions. The sorption behaviors of Zinc ions in these experiments under various conditions were examined and the following conclusions can be made:

1. The maximum sorption capacity and effect of N-HAP increases as pH increases from 4.50 to 7.50 and it has the best value of 1.310 and 1.562 mmol/g at pH=7.50 for 1537.6 nm and 47.6 nm particle sizes, respectively.
2. Sorption of Zinc ion onto N-HAP follows the second-order rate kinetics.
3. The Freundlich isotherm model is appropriate to describe the sorption of the Zn (II) ion on the N-HAP and it has a better fit than the Langmuir isotherm model.
4. In 47.6 nm particle sizes, these experiments show better maximum sorption capacity and more appropriate thermodynamic parameters.
5. Values of ΔG° show that the sorption of the Zn (II) ion onto N-HAP is a favorable spontaneous process
6. The values of S^* show that adsorption follows Shemisorptions
7. The values of ΔH° and ΔS° are 8.194 $\text{KJ}\cdot\text{mol}^{-1}$ and 39.96 $\text{KJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively, which indicate an endothermic sorption process and an increase in the randomness in the solid/solution interface during the sorption process.

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