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KINETIC, EQULIBRIUM, AND THERMODYNAMIC EVALUATION OF ZINC, COBALT, AND NICKEL IONS REMOVAL FROM AQUEOUS SOLUTION BY MODIFIED BIOMASS OF ASPERIGILLUS FLAVUS

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ABSTRACT

Heavy metal ions of Zn (II), Co (II), and Ni (II) can be toxic to humans and environment, thus it must be removed from wastewaters before discharge to water bodies. In the present study, the biomass of *Aspergillus flavus* was modified by calcium chloride and used to removal of heavy metal ions (nickel, cobalt and zinc) from aqueous solutions. The effect of different parameters such as initial pH, adsorbent dosage, contact time and temperature on the efficiency of adsorption process was studied. Pseudo-second model compared to the pseudo-first model has greater ability to describe the kinetic data. According to the correlation coefficient (R^2), Langmuir isotherm model was better described the isotherm behavior of the adsorption process. The maximum capacity for the adsorption of nickel, cobalt and zinc ions by the biomass of modified *Aspergillus flavus* was determined 32.258, 31.056 and 27.855 mg/g, respectively. ΔG°, ΔH°, and ΔS° parameters was showed that the biosorption of heavy metals by the adsorbent, is a possible, spontaneous and exothermic process.

KEYWORDS: **Biosorption, Modified *Aspergillus flavus*, Kinetic, Thermodynamic, Heavy metals**

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INTRODUCTION

Due to the rapid progress in industry, heavy metals were released extremely in the environment which causes the main concern.[1] Heavy metals, even at low concentrations are highly toxic when accumulate in living organisms which leads to the long or short term adverse events. [1-2] Different industries produce heavy metals, the most predominant are: mining and smelting, electrolysis, leather and nuclear energy industries, etc. We have three different types of heavy metal, including: toxic metals, precious metals, and radioactive metals.[3] According the World Health Organization (WHO), some metals such as, aluminum, chromium, cobalt, nickel, copper, cadmium, zinc, mercury, and lead are considered as toxic metals. [4] In order to prevent the prospective health events, various methods and techniques are existed for the removal of heavy metal ions from the environment. Among these methods the most practical are known as: chemical deposition, ion change, membrane filtration, electrolyte, reverse osmosis, solvent extraction and adsorption. [5-7] Among these processes, adsorption technique is considered the best owing to its cheapness, easiness and the high efficiency. [8-9] In this method various adsorbents are used to adsorb and remove heavy metal ions from aqueous solutions. Activated carbon is an example of common adsorbent for the recovery of municipal and industrial wastewater, but the high expenses of this substance made any special investigation appreciable for the detection of appropriate bioadsorbent. [10] Nowadays, in order to reduce the costs and operational process, special attention is given to the natural and organic material. The previous efforts regarding natural adsorbents include: olives, [11] activated carbon originated from nucleus of olive [12] and apricot, [13] waste tea, [14] fungal biomass *Pycnoporus sanguineus*, [15] *Aspergillus niger* and *Aspergillus flavus* [16] and *Rhizopus oryzae*[17-18]. In the present study in order to remove the zinc, cobalt and nickel ions, we used the modified biomass of *Aspergillus flavus*. Biomass of *A. flavus* seems to be a suitable bioadsorbent material, as it could be produced easily and economically by using facile fermentation methods with a high yield of biomass and growth media. We aimed to assess the effect of primary pH solution, adsorbent dosage, temperature and contact time on the efficiency of ions removal by the usage of modified biomass. The kinetic and equilibrium behavior of the adsorption process were also evaluated.

MATERIALS AND METHODS

1. Microorganisms and growth conditions

In this study, *Aspergillus flavus* was prepared from the Department of Microbiology, Bushehr University of Medical Sciences, Iran in the dry ice form. Then, it was cultured in the solid medium contains 40 g/L glucose, 10 g/L peptone, and 15 g/L agar, and kept in 4 ^{o}C. For biomass production, the fungi was cultured in a liquid medium containing: 120 g/L sucrose, 2 g/L NH_4Cl, 1g/L KH_2PO_4, 0.25 g/L $MgSO_4$.7 H_2O, 0.3 mg/L $FeSO_4$, 0.4 g/L $ZnSO_4$, 0.15 g/ L $MnSO_4$, 0.4 g/L $CuSO_4$. Afterward it was placed in an incubator at a temperature of 30 ^{o}C and rotation speed 200 rpm for a week. [19] Upon completion, the biomass of *A. flavus* was collected by filtration of liquid medium and washing several times with double distilled water. Henceforth it was placed in the oven at 70 ^{o}C for 24 h until dry, and finally it stored in plastic containers with lids at 4 ^{o}C.

2. Chemical modification

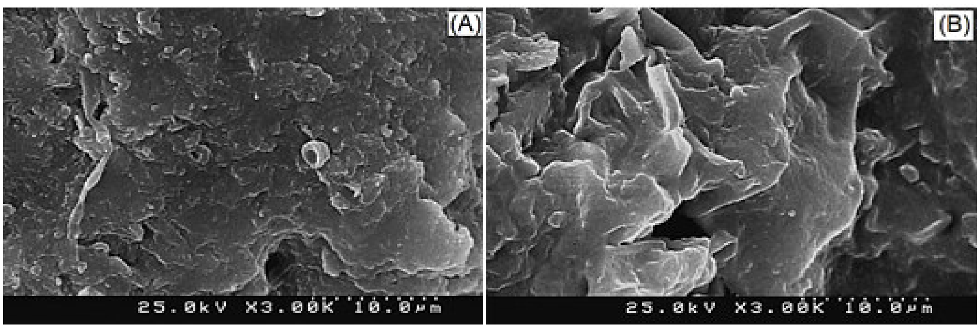
For this purpose, above biomasses was immersed in a solution of 2.0 M calcium chloride for 30 minutes. Then we separated the biomasses from the sodium hydroxide solution and washed it several times with double distilled water. The rinsed biomass put in autoclave for 30 minutes at 120 ^{o}C, and was dried at a temperature of 60 ^{o}C for 24 hours. [20] The dried biomass was ground by a home mill and sort by sieving by ASTM NO. 25 and then used for the tests.

3. Preparation of stock solution

To prepare a solution containing heavy metal ion Zn(II), Ni(II) and Co (II), we used nitrate salt [$Ni(NO_3)_2$. $4H_2O$, $Co(NO_3)_2$.$6H_2O$, $Zn(NO_3)_2$.$6H_2O$]. Stock solution with initial concentration of (1000 mg/L) was prepared by solving certain amount of the mentioned compounds in twice distilled water. To provide the soluble heavy metals with certain concentration 50 mg/L, stock solution was diluted by using double-distilled water.

4. Bio-adsorbent surface characteristics

To study surface changes of the fungus *A. flavus*, the scanning electron microscope (SEM, Hitachi S4160) was used. In order to capture images of the surface of the bioadsorbent, at first its surface was covered with a thin layer of gold under vacuum condition and then scanning electron microscopy were used. The obtained SEM images show the appearance of bioadsorbent surface. Vents and holes of different sizes can be seen in the fungi surface, are considered as an important factor to adsorb metal ions from aqueous solution by bioadsorbent. In Fig. 1, the surface of unmodified and modified *A. flavus*, as well as the surface of modified fungi after adsorption of heavy metal ions is shown. Also, the surface of adsorbent after addition of Zn, Co and Ni are shown in Fig. 1.



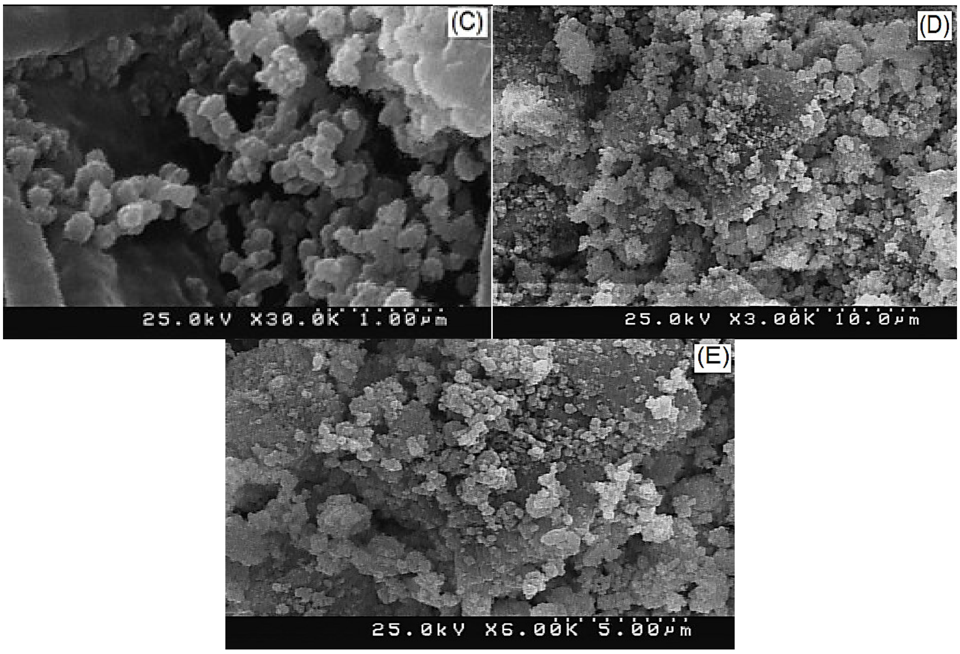


FIGURE 1
SEM images of Aspergillus flavus, A) before modification, B) after modification, C) after sorption of Zn (II) ion, D) after sorption of CO (II) ion, and E) after adsorption of Ni (II).

5. Experimental procedure
In order to determine the optimal conditions to adsorb heavy metals ions onto bioadsorbent, assay was carried inside of 250 ml Erlenmeyer flasks which contain a 100 ml solution with constant concentration (50 mg/L). To investigate the effect of pH on heavy metal ion adsorption efficiency, initial pH of the solution was set in a range of 2-8. To adjust pH in the desired range we used hydrochloric acid and sodium hydroxide solution 0.1 M. After determining the optimum pH in order to evaluate the effect of temperature and contact time on the adsorption efficiency of heavy metal ions, the process of adsorption was carried out in the temperature range 293.15 - 323.15 K , contact time 5- 150 min, pH optimum, mixing speed 200 rpm and adsorbent dose 4 g/L. Similarly, the effect of adsorbent dosage on the efficiency and capacity of heavy metal ions adsorption was conducted under the range 1-8 g/L, pH and other optimal conditions, so the best percent of adsorption has been reported as the optimal condition. To determine the amount of heavy metal ions remaining in the solution and adjusting the initial pH of solution, we used flame atomic adsorption spectrometry SpectrAA-10 Plus manufactured by Varian Company and digital pH meter Metrohm, respectively. In all cases the percentage of heavy metal ion biosorption (R%) and biosorption capacity (q_e) was calculated using the formula of 1 and 2:

$$R(\%) = \left(\frac{C_i - C_0}{C_i}\right) \times 100 \qquad (1)$$

$$q_e = \left(\frac{C_i - C_0}{W}\right) V \qquad (2)$$

where C_i and C_0 is the initial concentration and equilibrium concentration of metal ions (mg/L) respectively, V volume of solution (L), W is the weight of dry bioadsorbent (gr), R is adsorption percent of heavy metals ions, and q_e is ion adsorption capacity per gram of dry bioadsorbent (mg/g).

RESULTS AND DISCUSSION

1. Effect of pH
Initial pH is one of the important parameters in the process of adsorption that affects both chemical solution of heavy metals and the bioadsorbent surface. [21] The effect of initial pH on the adsorption efficiency of zinc, nickel and cobalt ions were studied under the pH range 2-9, temperature 293.15 K, contact time 60 min, bioadsorbent dosage 4 g/L, mixing rate 200 rpm and initial concentration of metal ions in the solution 50 mg/L. The result of the pH effect on the adsorption efficiency of heavy metal ions from aqueous solution is shown in Fig. 2.The maximum adsorption of metal ions nickel, zinc and cobalt were occurred in the pH of 5, 6 and 6, respectively, and the adsorption efficiency of nickel ions, cobalt and zinc in the optimal pH, were reported 92.11%, 95.1% and 93.21%, respectively. At low pH (<4) adsorption efficiency of heavy metal ions was very low, because the concentration of hydrogen ions in the aqueous solution is very high and hydrogen ions compete with heavy metal ions in this solutions in order to get onto the active sites of bioadsorbent. [22-23] As the result of active sites occupation by hydrogen ions (H^+), not enough surfaces were remained for the adsorption of heavy metal ions by bioadsorbent. Also, because the same charge of hydrogen ions with ions of heavy metals zinc, nickel and cobalt, repulsive force is created between them and this factor also prevents metal ions exposure to active sites of bioadsorbent. With increasing pH, the efficiency of metal ions adsorption by bioadsorbent are increased, since the increasing pH, competitive effects of hydrogen ions (H^+) is reduced as

well as especial groups such as hydroxyl, phosphate and amine in the adsorbent surface catch negative charge. [24] And also should be noted that by increasing the initial pH, the various hydrolysis groups will be appeared which can change the relationship of active sites in the cell wall. [25] Therefore, these factors can facilitate the adsorption of metal ions on the surface of bioadsorbent and increase the adsorption efficiency. But at high pH due to the presence of hydroxide ions (OH^-) in aqueous solution, metal ions combine with hydroxide ions to form a precipitate and this factor prevents the metal ion to contact the active sites of bioadsorbent and thus the efficiency of metals ion adsorption reduced.

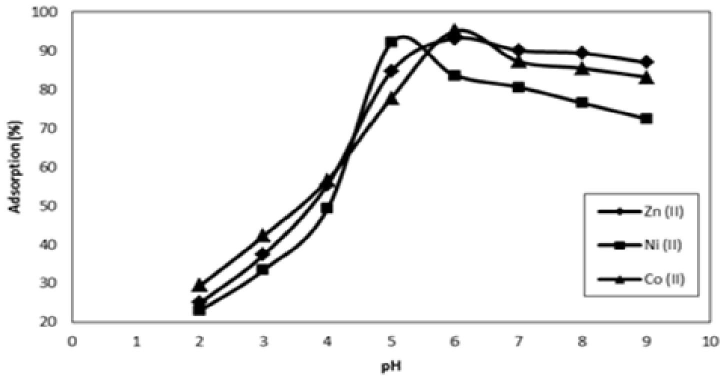


FIGURE 2
The effect of pH on the adsorption of zinc ion (II), Ni (II) and cobalt (II) by using Aspergillus flavus(Initial concentration of metalions: 50 mg/L, biomass dose: 4 g/L, contact time: 60 min, temperature: 293.15 K).

2. Effect of temperature and contact time on the adsorption efficiency

For this aim, the rate of adsorption is very important. Contact time is an important parameter to describe the practical use and the adsorption rate of the bioadsorbent. [1, 26] The results of the time effect on the efficiency of zinc, nickel and cobalt adsorption are shown in Figures 3, 4 and 5, respectively. According to the results, contact time augmentation, increased the efficiency of metal ions adsorption by the bioadsorbent of the fungus *A. flavus*. Metal ion adsorption process at the initial time of contact was performed with higher speed due to the presence of active sites on the surface and the cell wall of bioadsorbent. The balanced contact time for zinc, nickel and cobalt ions sorption, was determined at 60 min, 60 min and 80 min, respectively. And in the balanced contact time, the adsorption efficiency of zinc, nickel and cobalt, were reported 93.21%, 92.11% and 97.18%, respectively. Temperature is another crucial parameter in the adsorption of metal ions that affects the adsorption efficiency of metal ions. Results of the zinc, nickel and cobalt ions sorption by bioadsorbent are shown in Fig. 3, 4 and 5, respectively. By increasing the solution temperature from 293.15 K to 323.15 K, zinc, nickel and cobalt ions adsorption by bioadsorbent, were reduced from 93.21 to 85.34%, 92.11 to 80.23% and 97.18, to 89.2%, respectively. The results show that the zinc, nickel and cobalt ion adsorption by biomass of *A. flavus* is an exothermic reaction. Reducing the ion adsorption efficiency of zinc, nickel and cobalt by the use of mentioned bioadsorbent may be caused by detachment and the replacement of metal ions from bioadsorbent surface into the solution. [27] Thus the optimal temperature for the zinc, cobalt and nickel ions adsorption by the biomass of modified *A. flavus* fungus were determined 293.15 K.

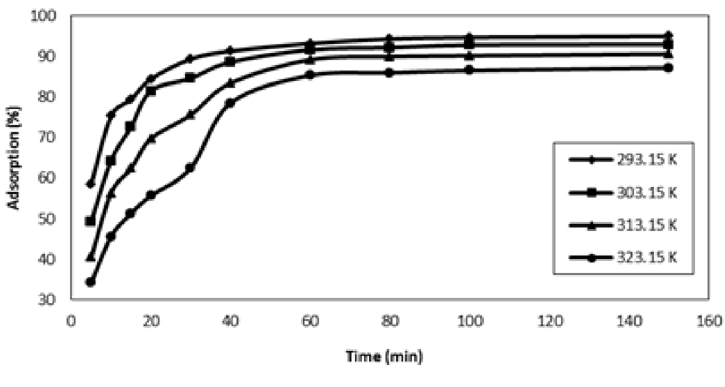


FIGURE 3
The effect of temperature and contact time on the efficiency of zinc ion adsorption (pH: 6, Metal concentration: 50mg/L, adsorbent dosage: 4 g/L).

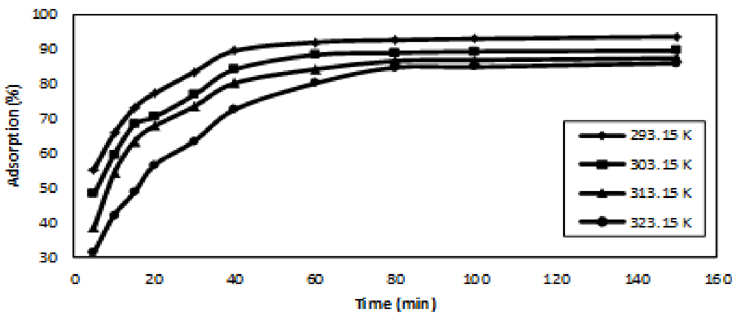


FIGURE 4
The effect of temperature and contact time on the efficiency of nickel ion adsorption (pH: 5, Metal concentration: 50mg/L, adsorbent dosage: 4 g/L).

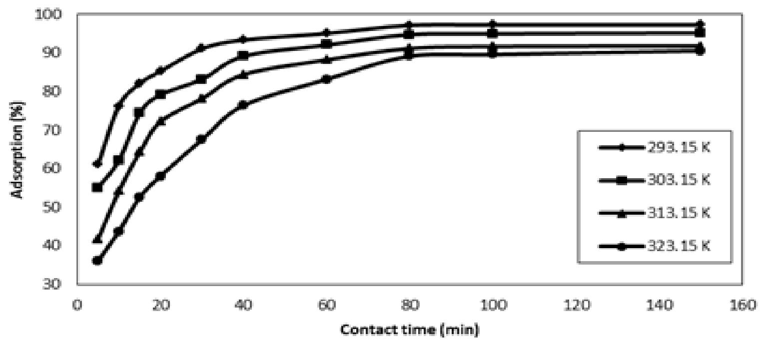


FIGURE 5
The effect of temperature and contact time on the efficiency of cobalt ion adsorption (Conditions: pH: 6, metal concentration: 50mg/L, adsorbent dosage: 4 g/L).

3. The effect of biomass concentration on adsorption efficiency

The effect of adsorbent dosage on the adsorption efficiency of nickel, zinc and cobalt ions were studied, in a various amount of adsorbent dosage ranging from 1 to 8 g/L with constant concentration of other parameters. The results show that with increasing adsorbent dose from 1 to 5 g/L, adsorption of zinc, nickel and cobalt ions increase from 72% to 96.8%, 68.41% to 95.18% and 74.17% to 97.41%, respectively. With the increasing amount of adsorbent dose, the number of active sites increases for zinc, nickel and cobalt ion adsorption, thus the adsorption efficiency of heavy metals increased from an aqueous solution with the use of biomass of *A. flavus*. After the adsorbent dosage 5 g/L, with increasing doses of adsorbent the adsorption efficiency of metal ions was not increased significantly, because by increasing of adsorbent dosage a large number of adsorbent active sites remain unsaturated. [21] Thus, according to the results suitable adsorbent dosage, for the recovery of heavy metal ions from an aqueous solution was determined to be 5 g/L.

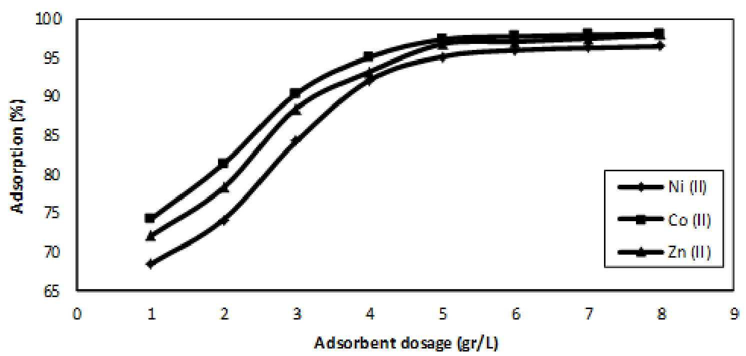


FIGURE 6
The effect of adsorbent dosage on the adsorption efficacy of nickel, cobalt and zinc ($pH_{optimum}$, tempature: 293.15 K, time: 60min, metal concentration: 50 mg/L).

4. Adsorption isotherm study

In order to study the isotherm behavior of the adsorption process, several isotherm models can be used. Isotherm models that are commonly used consist of Freundlich and Langmuir isotherm model. Adsorption isotherm study by two methods is briefly described below.

4.1. Langmuir isotherm

Langmuir isotherm model is widely used to describe the behavior of metals bioadsorbent. Langmuir isotherm model assumes that the heavy metals ions are adsorbed only to the active sites on the surface of bioadsorbent, so adsorption was limited to the layer on the surface of bioadsorbent, thus an even adsorption take place. In addition, we assume that bioadsorber superficial lateral sites have the equal tendency for the mentioned metal ion adsorption. Langmuir linear model is as follows: [2, 4]

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right)\frac{1}{C_e} \qquad (3)$$

where, C_e refers to the concentration of metal ions at equilibrium (mg/L), q_e (mg/g) is the amount of metal ions adsorbed per gram of adsorbent in equilibrium. q_{max} and b are referred to the adsorption capacity (mg/g) and energy (L/g) respectively, which considered as the constant parameters in the Langmuir model. By measuring the slope and intercept of linear Langmuir equation, $1/q_e$ was obtained based on $1/C_e$. Other important parameter in Langmuir equation is R_L. R_L represents the state and characteristics of the isotherm adsorption model. If $R_L > 1$, $R_L = 0$, $R_L = 1$ and $0 < R_L < 1$ the process considered as undesirable, irreversible, linear and good, respectively. [2, 4] R_L is determined as follows by equation: [10]

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

where, C_0 (mg/L) refers to the initial concentrations of lead ions in aqueous solution. Linear relationship between $1/q_e$ versus $1/C_e$ to adsorb metal ions nickel, cobalt and zinc are shown in Figure 7a-c. R_L value for the ions adsorption of nickel, cobalt and zinc were determined 0.9349, 0.9419 and 0.951 respectively, that indicate a high potential of Langmuir model to describe the isotherm behavior of process. The amount of metal ion adsorption capacity of nickel, cobalt and zinc by using the biomass of the modified fungus *A. flavus*, was determined 32.258 mg/g, 31.056 mg/g and 27.855mg/g, respectively. R_L value for the ions adsorption of nickel, cobalt and zinc were determined 0.119، 0.064 and 0.0664, respectively which states that the heavy metal ions adsorption process by the biomasses of modified fungus is desirable ($0<R_L<1$). Table 1 are listed constants and other parameters of the Langmuir isotherm model, for heavy metal ions nickel, cobalt and zinc adsorption by biomass of modified *A. flavus* from aqueous solution.

4.2. Freundlich isotherm

Freundlich isotherm model is an empirical relationship, can be used as a criterion for describing the isotherm behavior of bioadsorbent in the heavy metal ion adsorption process from aqueous solutions. This model is used to describe the heterogeneous and multi-level adsorption process. [28] Freundlich isotherm model assumes that heavy metal ions penetrate into the lower levels of adsorbent, and adsorption occurs unevenly in non-uniform surfaces. Linear form of Freundlich model is as follows:

$$Lnq_e = LnK_f + \frac{1}{n}LnC_e \qquad (5)$$

where, q_e, equilibrium adsorption capacity (mg/g), C_e equilibrium concentration of metal ions in solution (mg/L), K_f and n are constant parameters of Freundlich model that demonstrate the relationship between adsorption capacity and adsorption rate. To determine the parameters of 1/n and K_f, the $\ln q_e$ draw against $\ln C_e$. n represents the interactions between the bioadsorbent and the metal ion, in addition its amount have been reported in the range of 1-10. [28] Value of n represents the physical and chemical adsorption process. If n = 1 it is the linear adsorption process, if n> 1 it is desirable physical adsorption process, and if n <1 it is expressed as chemical and optimal adsorption process. [5] Value of n for the adsorption of nickel, cobalt and zinc ions by the biomass of modified *A. flavus*, were determined 1.65, 1.8 and 1.79 respectively, which indicated the desirable and physical adsorption process. In the figure 8a-c, linear relationship is shown between $\ln q_e$ and $\ln C_e$ for the adsorption of nickel, cobalt and zinc ions onto biomass of modified *A. flavus* fungi. Correlation coefficient (R^2) for the adsorption of metal ions, nickel, cobalt and zinc determined 0.9127, 0.9392 and 0.9342 respectively. Table 1 are listed constants and other parameters of the Freundlich isotherm model, for nickel, cobalt and zinc ions adsorption by biomass of modified *A. flavus* from aqueous solution.

Table 1

The value of parameters for each isotherm models used in this study.

Isotherms	Parameters	Metal ion		
		Ni(II)	Co(II)	Zn(II)
Langmuir	q_{max} (mg/g)	32.258	31.056	27.855
	b (l/mg)	0.147	0.292	0.281
	R_L	0.119	0.064	0.0664
	R^2	0.9349	0.9419	0.951
Freundlich	n	1.65	1.8	1.79
	K_f (mg/g)	4.846	7.168	6.346
	R^2	0.9127	0.9392	0.9342

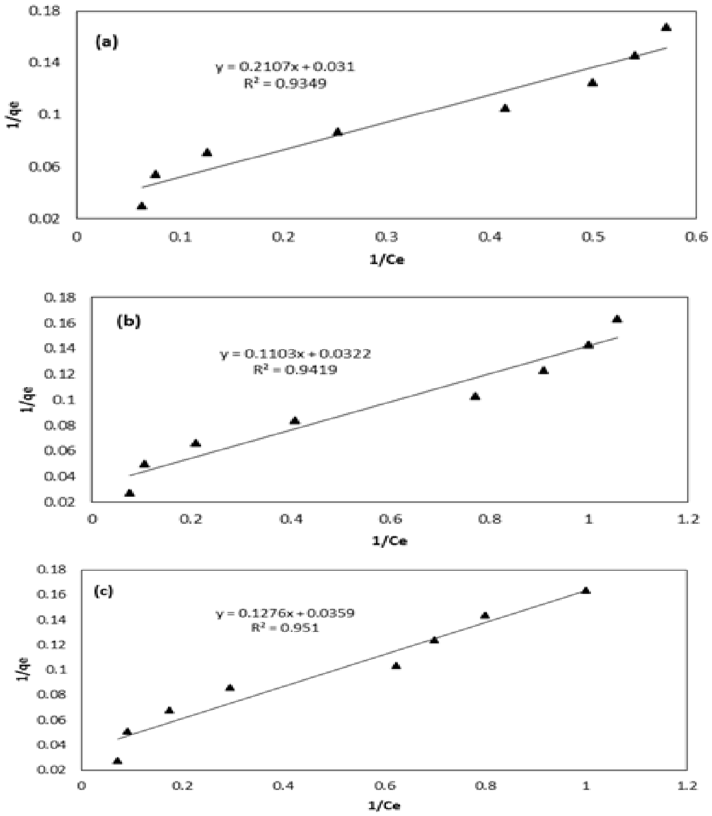


FIGURE 7

Langmuir isotherm plots for adsorption (a) Ni(II) ions, (b) Co(II) ions and (C) Zn(II) ions on biomass A. flavus fungi (initial concentration ions:50 mg/L, time:60 min, temperature:293.15 K, adsorbent dosage:1-8 g/L).

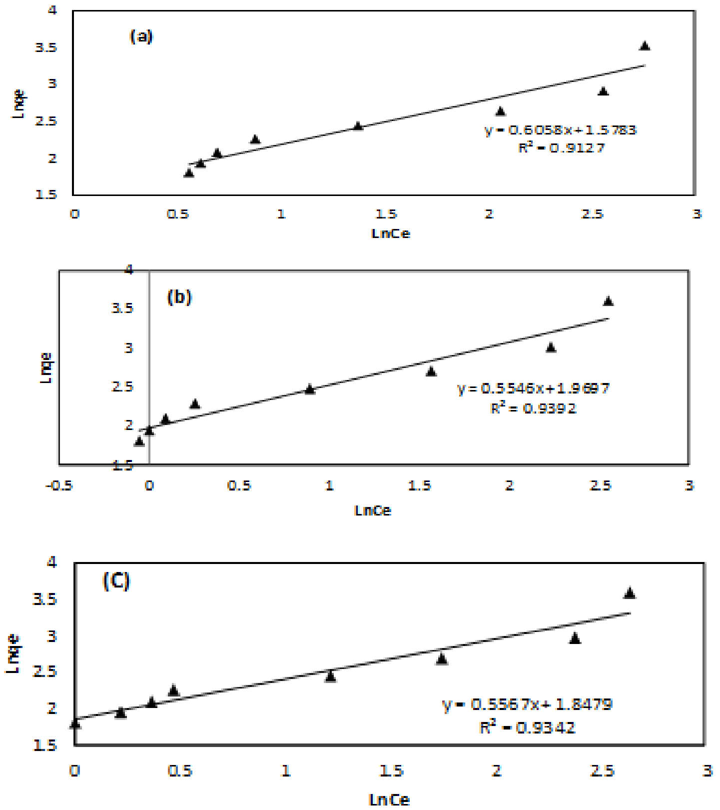


FIGURE 8

Freundlich isotherm plots for adsorption (a) Ni(II) ions, (b) Co(II) ions and (C) Zn(II) ions on biomass A. flavus fungi (initial concentration ions:50 mg/L, time:60 min, temperature:293.15 K, adsorbent dosage:1-8 g/L).

5. Adsorption kinetic study

Sorption kinetics give information about sorption capacity and rate of the biosorption process occurs [1]. It is important to determine appropriate kinetic model that provides best fit with the experimental data. A lot of kinetic models have been employed to describe the sorption kinetic. For kinetic behavior investigation, various adsorption kinetic models exist, however the most common models are pseudo-first and pseudo-second version, which is used in many previous studies. In this study in order to describe the kinetic behavior of the biomass of modified *A. flavus* to adsorb ions of heavy metals nickel, cobalt and zinc from aqueous solutions, we used pseudo-first and pseudo-second kinetic models.

5.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model is one of the most common and most widely used in describing the kinetic behavior of heavy metal ion adsorption by bioadsorbent. Equation (6) shows the linear relationship of pseudo-first model that was used in this study: [29,30]

$$Ln(q_e - q_t) = Lnq_e - k_1 t \qquad (6)$$

where, q_e is the amount of ion adsorbed by the adsorbent in equilibrium (mg/g) per gram of adsorbent, q_t is the amount of ions adsorbed (mg/g) per gram of adsorbent at any time and k_1 is the constant of adsorption (1/min). In (q_e-q_t) versus t was drawn, in order to calculate the specific adsorption rate (K_1) and other parameters. The results of equilibrium process of ion adsorption nickel, cobalt and zinc are reported in Tables 2a-c, respectively. According to reports, the adsorption capacity determined by pseudo-first-order kinetic model ($q_{e.caL}$), has a smaller amount than the capacity determined by adsorption assay ($q_{e.exp}$). It can be stated that the pseudo-first model, does not have a good ability to describe the kinetics behavior of ion adsorption of heavy metals nickel, cobalt, and zinc. The correlation coefficient (R^2) of ion adsorption process of nickel, cobalt, and zinc in the temperature range 293.15 K-323.15 K has been determined in the range of 0.9664 to 0.9906, from 0.9609 to 0.9863 and from 0.9655 to 0.9872, respectively.

5.2 Pseudo-second-order kinetic model

Pseudo-second-order kinetic model kinetic model is another common method to describe the kinetic behavior of adsorption process. Linear form of pseudo-second-order kinetic model is shown below[27]:

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \frac{1}{q_e} t \qquad (7)$$

where q_e is the amount of ions adsorbed at equilibrium (mg/g) per gram of adsorbent, q_t is the amount of ions adsorbed (mg/g) per gram of adsorbent at time t, K_2 is the constant rate of pseudo-second order kinetic equation ($g.mg^{-1}.g^{-1}$). The initial adsorption rate ($mg\ g^{-1} min^{-1}$) for the pseudo-second-order kinetic equation is determined as follow by the equation (8)[27]:

$$h = K_2 q_e^2 \qquad (8)$$

Linear relation t/q_t versus t is shown in the Figure 9 a-c for ion adsorption of nickel, cobalt and zinc, respectively. The q_e, K_2 and h for the adsorption of ions nickel, cobalt and zinc in the temperature range of 293.15 K-323.15 K was determined from the slope and intercept of linear model t/q_t versus t. The results show that by temperature augmentation, the amount of initial adsorption rate (h) for the adsorption of ions nickel, cobalt and zinc reduced, while the maximum adsorption rate was determined at 293.15 K. The adsorption rates for nickel, cobalt and zinc were reported 2.791, 4.197 and 4.133 $mg\ g^{-1} min^{-1}$, respectively. According to our data (Table 2a-c), the amount of adsorption capacity determined by pseudo-second-order kinetic model ($q_{e.cal}$) has small discrepancies with the amount determined by adsorption assay ($q_{e.exp}$). It stated that the pseudo-second model, have a good ability to describe the kinetic behavior of the process. Table 2a-c is listed Constants and other parameters determined by the pseudo-second-order kinetic model for nickel, cobalt and zinc ions adsorption with *A. flavus* biomass.

Table 2a

Parameters calculated using pseudo-first-order and pseudo-second-order models for Ni(II) ions adsorption with A. flavus biomass.

Kinetic model	Parameters	Temperature			
		293.15 K	303.15 K	313.15 K	323.15 K
Pseudo-first-order	$q_{e.cal}$	4.79	6.89	6.81	9.09
	K_1	0.0449	0.0578	0.0486	0.0444
	$q_{e.exp}$	11.721	11.206	10.94	10.65
	R^2	0.9664	0.9906	0.9887	0.9784
Pseudo-second-order	$q_{e.cal}$	12.12	11.709	11.534	11.806
	K_2	0.019	0.016	0.013	0.0069
	$q_{e.exp}$	11.721	11.206	10.94	10.65
	h	2.791	2.193	1.729	0.962
	R^2	0.9997	0.9994	0.9996	0.9983

Table 2b
Parameters calculated using pseudo-first-order and pseudo-second-order models for Co(II) ions adsorption with A. flavus biomass.

Kinetic model	Parameters	Temperature			
		293.15 K	303.15 K	313.15 K	323.15 K
Pseudo-first-order	$q_{e.cal}$	7.121	6.786	9.116	9.714
	K_1	0.0733	0.0548	0.0591	0.0448
	$q_{e.exp}$	12.165	11.906	11.481	11.325
	R^2	0.9609	0.9843	0.9863	0.9805
Pseudo-second-order	$q_{e.cal}$	12.468	12.376	12.136	12.376
	K_2	0.027	0.0168	0.0121	0.0068
	$q_{e.exp}$	12.165	11.906	11.481	11.325
	h	4.197	2.573	1.782	1.041
	R^2	0.9999	0.9997	0.9995	0.9981

Table 2c
Parameters calculated using Pseudo-first-order and Pseudo-second-order models for Zn(II) ions adsorption with A. flavus biomass.

Kinetic model	Parameters	Temperature			
		293.15 K	303.15 K	313.15 K	323.15 K
Pseudo-first-order	$q_{e.cal}$	3.892	5.603	7.541	9.067
	K_1	0.048	0.0547	0.0536	0.0499
	$q_{e.exp}$	11.875	11.625	11.3325	10.844
	R^2	0.9841	0.9872	0.9771	0.9655
Pseudo-second-order	$q_{e.cal}$	12.15	12.03	11.99	11.92
	K_2	0.028	0.02	0.01226	0.0075
	$q_{e.exp}$	11.875	11.625	11.3325	10.844
	h	4.133	2.894	1.762	1.065
	R^2	0.9999	0.9997	0.9992	0.996

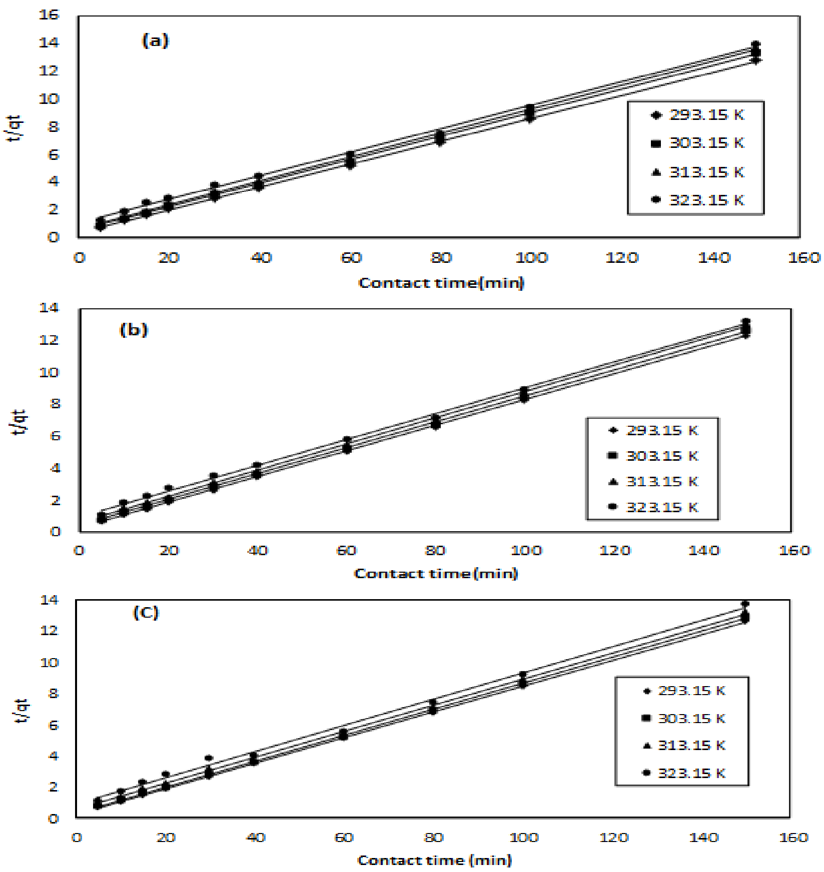


FIGURE 9
Pseudo-second order kinetic plots for the adsorption (a) Ni(II), (b) Co(II), and (C) Zn(II) ions on biomass A. flavus.

6. *Thermodynamic parameters*

To study the thermodynamic behavior of heavy metals ions adsorption from aqueous solution, thermodynamic parameters include the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) was determined by using the following equation[14]:

$$\Delta G^\circ = -RT\,Ln K_D \qquad (9)$$

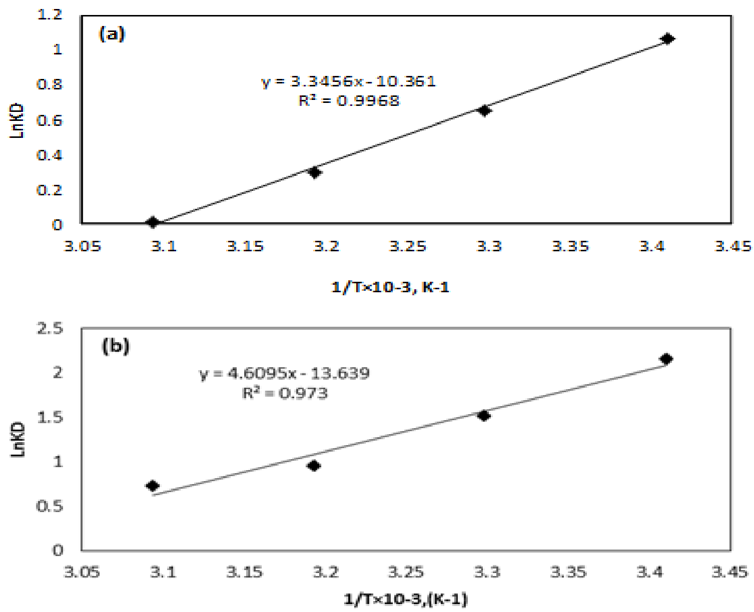
where R refers to universal gas constant (8.314 J/(mol.K)), T is temperature by Kelvin (K) and K_D (q_e/C_e) is coefficient distribution. Also, ΔH° and ΔS° determine from equation 10.

$$Ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (10)$$

According to equation (10), ΔH° and ΔS° parameters of metal ions adsorption are determined by calculating the slope and intercept of the graph $\ln K_D$ versus 1/T (Fig. 10a-c). The thermodynamic parameters for the adsorption of heavy metal ions have been determined in the temperature range of 293.15-323.15K. The results have been reported in Table 3. Gibbs free energy in various temperatures 293.15K, 303.15K, 313.15K and 323.15 K was determined -2.61, -1.649, -0.7744 and -0.03877KJ /mol for nickel ion adsorption, -5.248, -3.823, Negative values of ΔH° indicate that the adsorption of ions nickel, cobalt and zinc, is exothermic in the temperature range 293.15K-323.15K. By comparing the ΔH° values of metal ion adsorption, it can be stated that the cobalt ion adsorption compared to the adsorption of nickel and zinc ions needs less energy. ΔS° value was -2.4884 and - 1.948 KJ/mol for cobalt ion adsorption, and -3.005, -2.556, -1.904 and -1.008 KJ /mol for zinc ions adsorption, respectively. Negative values of ΔG°, indicates that the adsorption process of metal ions, nickel, zinc and cobalt are thermodynamically feasible. ΔG° values decreased with increasing temperature, which indicates the degree of feasible spontaneous process decreases with increasing temperature. ΔH° was determined for ion adsorption of nickel, cobalt and zinc -0.0278, -0.0383 and -0.02239 KJ/mol, respectively. determined in the temperature range 293.15- 323.15K, for the adsorption of nickel, cobalt and zinc ions:-86.141, -113.39 and -65.7787J/mol.K, respectively. ΔS° negative value indicates that the random collisions between metal ions in the solution with the solid surface during the biosorption process reduced. [26]

Table 3.
Values of thermodynamic parameters for adsorption of Ni(II), Co(II) and Zn(II) with A. flavus fungi.

Metal ions	T (K)	ΔG°(KJ/mol)	ΔH°(KJ/mol)	ΔS°(J/mol.K)
Ni(II)	293.15	-2.61	-0.0278	-86.141
	303.15	-1.649		
	313.15	-0.7744		
	323.15	-0.03877		
Co(II)	293.15	-5.248	-0.0383	-113.39
	303.15	-3.823		
	313.15	-2.4884		
	323.15	-1.948		
Zn(II)	293.15	-3.005	-0.02239	-65.7787
	303.15	-2.556		
	313.15	-1.904		
	323.15	-1.008		



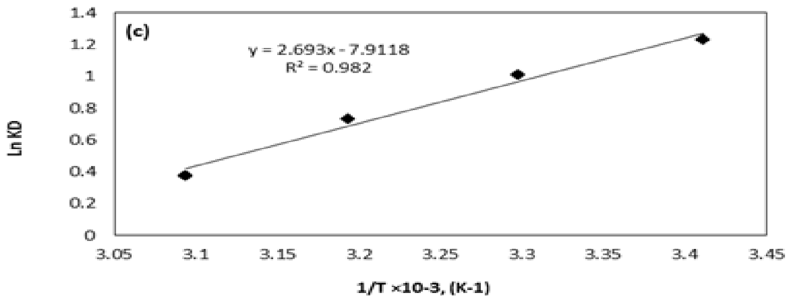


FIGURE 10

Plot of lnK_D versus 1/T for the estimation of thermodynamic parameters for biosorption of (a) Ni(II), (b) Co(II) and (c) Zn(II) onto A. flavus biomass.

CONCLUSION

In the present study, the biomass of modified *Aspergillus flavus* was used for recovery and removal of heavy metal ions nickel, cobalt and zinc from aqueous solution. We examined the effect of various parameters such as initial pH of solution, adsorbent dosage, temperature and contact time on the adsorption efficiency of metal ions. Among these parameters the initial pH had a significant impact on the adsorption efficiency heavy metal ions. Efficiency and removal of nickel, cobalt and zinc ions from aqueous solution increased with increasing the temperature, contact time, adsorbent dose and initial pH. Due to the R^2 value as well as comparison of adsorption capacity determined by adsorption assays ($q_{e.exp}$) to the capacity set by the kinetic models ($q_{e.caL}$), it can be stated that the kinetic models like pseudo-second model compared to the pseudo-first model has greater ability to describe the kinetic behavior. In order to study the isotherm behavior of metal ions adsorption process, Freundlich and Langmuir isotherm models were used. The maximum adsorption capacity indicated that the nickel ion adsorption capacity by biomass of modified *A. flavus* was higher compared to other ions. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° set for the uptake of the metal ions (Ni (II), Co (II) and Zn (II)) by the modified fungus indicated that the process is feasible and proceed spontaneously. By temperature augmentation, the degree of feasible spontaneous process decreases. The results showed that the biomass of modified *A. flavus* can be used as low-cost, accessible, efficient and effective bioadsorbent for retrieval and removal of heavy metals ions Ni (II), Co (II) and Zn (II) from aqueous solutions.

CONFLICT OF INTEREST

Conflict of interest declared none.

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