Solid-Phase Separation and Green Removal of Amprolium Hydrochloride Veterinary Drug from Aqueous Media Using *Dolomiaea Costus* Roots as New Biosorbent

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Abstract: The roots of the *Dolomiaea costus* (SCO) plant were used as a new, low-cost, eco-friendly, and efficient biosorbent for the removal of Amprolium hydrochloride (AMP) antibacterial veterinary drug residues from aqueous media. The effect of different parameters, such as the initial concentration of AMP, pH, contact time, adsorbent dosage, and temperature, was investigated. The results showed that the best removal of the AMP drug by SCO was reached at a pH of 3.6 at a contact time of 80 min by a sorbent dosage of 0.04 g at a temperature of 45°C. Adsorption isotherm studies indicated that the AMP removal correlates more with the Freundlich isotherm with $R^2 = 0.991$. The maximum adsorption capacity has reached 83% based on the adsorption isotherm studies. The kinetics studies showed that adsorption follows a pseudo-second-order model with $R^2 = 0.999$. The thermodynamic studies showed that the adsorption process of AMP on SCO is spontaneous in nature and exothermic, with an increase in randomness during the adsorption.

Keywords: Amprolium HCl; *Saussurea costus*; Biosorption; Adsorption isotherm; Kinetics studies; Thermodynamics studies.

1. Introduction

Several veterinary pharmaceuticals, particularly the antibacterial antibiotic Amprolium hydrochloride (AMP), have been demonstrated to have long-lasting adverse effects on various species, including humans [1]. AMP is a pyrimidine-derivative that is added to poultry feed to restrain protozoan coccidian growth [2], to stop sporulation of coccidial oocysts of different *Eimeria* species [3], and to decrease the degree of illness brought on by *Sarcocystis tenella* in sheep and by *Sarcocystis cruzi* in cattle [4]. AMP exists as a cationic species in aqueous medium [2]. AMP is a thiamine analog with the chemical structure 1-[(4-Amino-2-propyl-5-pyrimidinyl) methyl]-2-picolinium chloride monohydrochloride ($C_{14}H_{19}N_4Cl.HCl$, M.Wt. = 315.24) (Fig. 1) [5]. The majority of AMP drug is being excreted intact in urine and feces since it is poorly absorbed in the animal's gut [6], which means that the use of these wastes as natural fertilizers can be another source of pollution of soil and water, which, in turn, affects plants, animals, and humans as well as the aquatic organisms [7].

The spread of bacteria that are resistant to antibiotics may be facilitated by residual veterinary pharmaceutical drugs in different ecosystem matrices, which may ultimately reduce the clinical or veterinary effectiveness of antibiotics [8]. Several analytical techniques can utilized to determine Amprolium hydrochloride, including UV-spectrophotometry [9,10], HPLC [11,12], atomic spectrometry [13], GC [14], and other electrochemical methods [15]. Few studies were carried out for the adsorptive removal of AMP from aqueous media [16].

Numerous approaches have been established for treating and removing pharmaceutical residuals from aqueous media. These approaches include chemical methods like oxidation, physical procedures such as adsorption and ion exchange, and biological processes such as aerobic degradation [17]. Some of these techniques are costly, time-consuming, and efficient enough to put a new burden on the ecosystem. The adsorption method is considered the most effective way to remove pollutants of veterinary drugs from water due to its affordability, simple design, and ease of operation.

In recent years, several studies have been carried out to develop eco-friendly, low-cost, and green biosorbents for the remediation of urban and industrial aqueous effluents before entering the ecosystem, including removing pharmaceutical drug residues. Several biosorbents have been used to remove such harmful chemicals, including *Pomegranate* peels [18,19], *Moringa stenopetala* seeds [20], *Cherry* seeds [21], and activated bamboo's charcoal [22]. In the current study, *Saussurea costus* was used as a biosorbent to remove a pharmaceutical drug from aqueous media for possible application in the remediation of small-scale polluted aqueous effluents. *Dolomiaea costus* plant, also known as *Saussurea costus* (SCO), is commonly named Costus or Indian Costus. The roots and roots' oil of Costus has become an essential natural medicine for the pharmaceutical-free treatment of several diseases [23]. The wide availability and affordable price of the Costus roots in some developing eastern countries may make them a suiFi eco-friendly option for the removal, or at least the reduction, of the harmful residual levels of the widely used AMP veterinary drug from small-scale industrial aqueous effluents before discharging in the ecosystem. For this purpose, the impact of several variables, including solution's pH, adsorbent dose, contact time, and temperature, were studied to remove AMP drug residues from aqueous media. The adsorption isotherm, kinetics, and thermodynamics were also studied to elucidate the experimental results further.
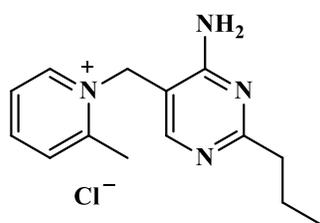
Figure 1. The chemical structure of Amprolium HCl (AMP) veterinary antibacterial drug

2. Experimental

2.1. Materials
The dried roots of *Saussurea costus* (SCO) (Fig. 2) were obtained from a local herbal market in Saudi Arabia. The National Organization provided amprolium hydrochloride ($C_{14}H_{19}N_4Cl \cdot HCl$) > 98% from Sigma-Aldrich for Drug Control and Research (NODCAR, Cairo, Egypt). All reagents used were of analytical grade and were purchased from Sigma Chemical Co. To create a 100-ppm stock solution of AMP, 0.025 g of the drug was dissolved in 250 ml of deionized water. A series of diluted solutions was prepared from the stock solution. All solutions were prepared using deionized water. The laboratory glassware was soaked in chromic acid solution overnight before being utilized.

Figure 2. The roots of the *Saussurea costus* plant

2.2. Instrumentation
UV–visible spectrophotometer (Thermo Scientific Genesys 10S) was used for spectrophotometric measurements with matching glass cells (10 mm). The pH of the aqueous solutions was measured using a pH meter with an Ag/AgCl electrode (Hanna-Instruments HI 221). An automated shaker (Heathrow Scientific HS120460) was used for batch experiments. The morphology of the sorbent's surface was characterized using a scanning electron microscope (SEM, JEOL1400, Japan).

2.3. The Preparation of Biosorbent
The *Saussurea costus* (SCO) roots were carefully washed several times with double-distilled water to remove dust and other undesired contaminants, then dried, grounded, and sieved.

2.4. Batch Technique
To construct calibration curves, 0.025 g of AMP drug (100 ppm) was dissolved in 20 ml of deionized water. Then the volume of solution was completed to 250 ml by adding deionized water. Different concentrations

(1 - 90 ppm) were prepared from the stock solution. The absorbance measurement of AMP was detected by using a spectrophotometer at λ_{max} 290 nm against a blank. The pH of the solutions was adjusted within the range of 3.0 - 8.0 by mixing 2.5 ml of AMP solutions (100 ppm), and 2.5 ml of acetate and phosphate buffer and shaking with 0.1 g of *Saussurea costus* (SCO) roots for 30 min. The remaining drug was spectrophotometrically determined. Also, the effect of contact time on the removal of AMP drug was determined by adding 0.04 g of SCO roots to 2.5 ml of AMP (100 ppm) and mixing at a pH of 3.6 with shaking at different interval periods of 15 to 120 min. The effect of the sorbent's amount was determined by adding 2.5 ml of buffer at a pH of 3.6 to 2.5 ml of AMP (100 ppm) while mixing with variable amounts of SCO roots (0.01 - 0.4 g). The effect of temperature was studied between 40-100°C by applying the same procedure detailed above. The remaining AMP drug residues in the solution were spectrophotometrically determined against a blank. The sorption percentage was estimated using Equation 1 [16]:

$$R\% = \frac{Co - Ct}{Co} \times 100 \qquad \text{Eq. 1}$$

Where C_o and C_t are the initial and final concentrations of the AMP drug adsorbate in liquid phase (mg/l), respectively.

2.5. Adsorption Isotherms, Kinetics and Thermodynamics Studies

The adsorption isotherm study procedure was carried out using the following optimal adsorption conditions: 0.04 g SCO sorbent on 2.5 ml of AMP (100 ppm) with 2.5 ml of buffer at a pH of 3.6 and shaking for 15 min at 45°C. The same procedure was applied for the kinetics study with 15 to 120 min contact time intervals. For the thermodynamics study, a temperature range of 40 to 100°C was investigated while applying the same procedure. The AMP drug's absorbance measurement was detected using a spectrophotometer at λmax of 290 nm against a blank [24] for all the studies.

3. Results and Discussions

3.1. The Morphology of The Sorbent's Surface

The surface morphology of *Saussurea costus* (SCO) sorbent was examined using a scanning electron microscope (SEM) with an accelerating voltage of 15 kV. The SEM image in Fig. (3a) shows that the SCO surface pores before adsorption had diameters in the micrometer (μm) range with heterogeneous surface morphology and various randomly distributed pore sizes. Fig. (3b) shows the surface morphology changes of SCO roots after the adsorption of the AMP drug, indicating that most of the surface pores were filled with the adsorbed material.
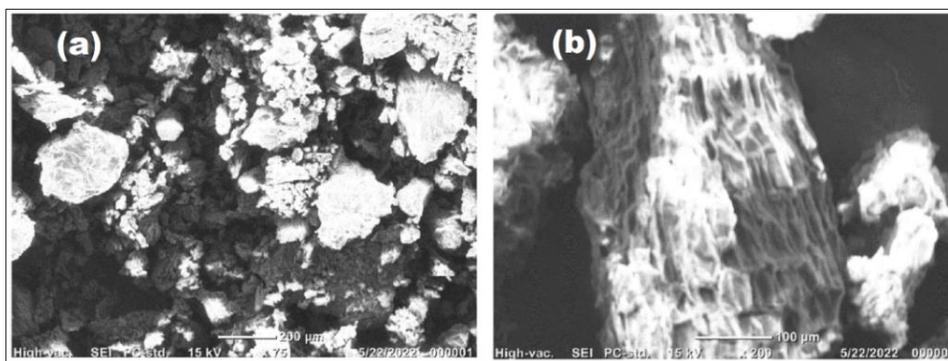
Figure 3. SEM images of *Saussurea costus* roots: (a) before absorption and (b) after absorption of AMP drug

3.2. The Effect of pH

The effect of the solution's pH was determined by adjusting the pH within the range of 3.0 - 8.0 while measuring the absorbance at 290 nm. The results show that the pH increases to reach maximum removal of AMP by Costus roots at a pH of 3.6 and then starts to decrease gradually as shown in Fig. 4. The adsorption mechanism is probably encouraged by a potential electrostatic interaction of the adsorbate's cationic species with the sorbent's negative surface sites, specifically the (OH) groups [25]. This can explain the decrease in the removal of AMP when the pH increases, where the interaction between AMP and [OH-] increases on the expense of interaction with SCO-negative surface sites [26,27]
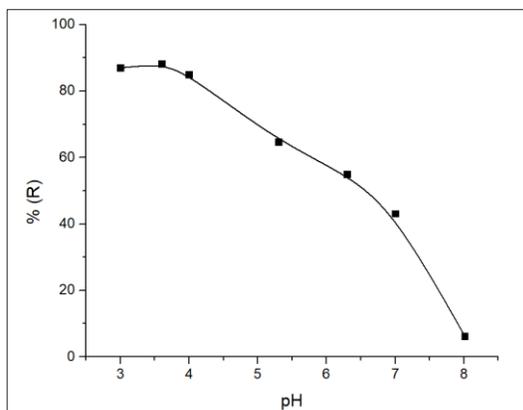
Figure 4. Effect of pH on the removal of AMP drug using SCO roots biosorbent
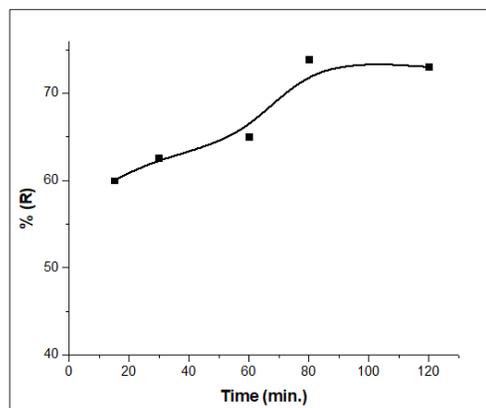
Figure 5. Effect of contact period on the adsorption of AMP drug by SCO roots

3.3. The Effect of Contact Time

The effect of contact time between sorbent and sorbate was studied within a 15 - 120 min range at the optimal pH value of 3.6. The results are shown in Fig. 5. The removal of the AMP by SCO roots biosorbent peaked at a contact period of 80 min before starting to decline. The decrease in removal after that period is probably attributed to the decrease in the number of available vacant sites on adsorbent surfaces [19,28].

3.4. The Effect of Sorbents Dosage

The effect of the amount of sorbent within the range of 0.01 - 0.4 g of SCO roots per 2.5 ml of AMP drug solution (100 ppm) was studied at the optimal pH value of 3.6. The results are shown in Fig. 6. The removal of AMP increased with the amount of sorbent until 0.04 g after which no further increase was detected. This could be attributed to particle aggregation upon increasing the sorbent dosage [29].
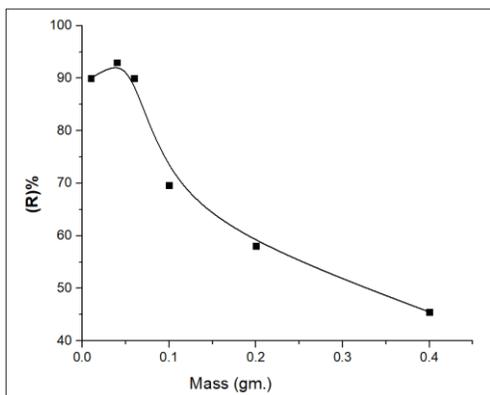
Figure 6. Effect of dosage of SCO roots sorbent on the removal of AMP from aqueous media
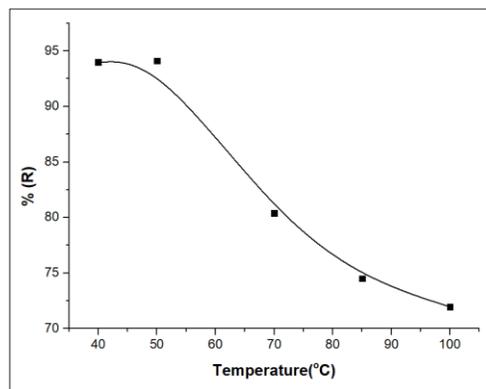
Figure 7. Effect of temperature on the removal of AMP from aqueous media by SCO roots

3.5. The Effect of Temperature

The effect of temperature was studied within the 40-100°C range at optimal removal conditions. The results are shown in Fig. 7. The removal of AMP has decreased with increasing temperature, which could be attributed to the reduced adsorption feasibility at high temperatures [30]. The optimal temperature for the removal of AMP using SCO was found to be 45°C.

3.6. Adsorption Isotherm

The effect of concentration of AMP drug within the range of 30 - 100 ppm was studied. When the initial concentration of AMP drug increased, the amounts of

AMP removal also increased, as shown in Fig. 8. The results indicate that the removal of AMP is highly dependent on its initial concentration [31]. The Langmuir and Freundlich isotherm models examined the experimental results. According to the Langmuir isotherm model, monolayer adsorption can only occur at a limited number of specific homogenous sites [26,32]. The non-linear expression of Langmuir isotherm model can be illustrated by equation 2 [29]:

$$C_e/q_e = 1/q_m b \ + \ (1/q_m)C_e \qquad \text{Eq. 2}$$

Where C_e is the concentration of AMP drug solution at equilibrium (mg/l), q_e is the corresponding adsorption

capacity of AMP per unit mass of SCO sorbent (mg/g), q_m is the maximum amount of adsorbed AMP per unit mass of SCO sorbent (mg/g), and b (l/mg) is the Langmuir constant related to the energy of adsorption.

The plot of C_e/q_e versus C_e gives a straight line with a slope equal to $1/q_m$ and an intercept similar to $1/q_m b$, respectively [27,33].
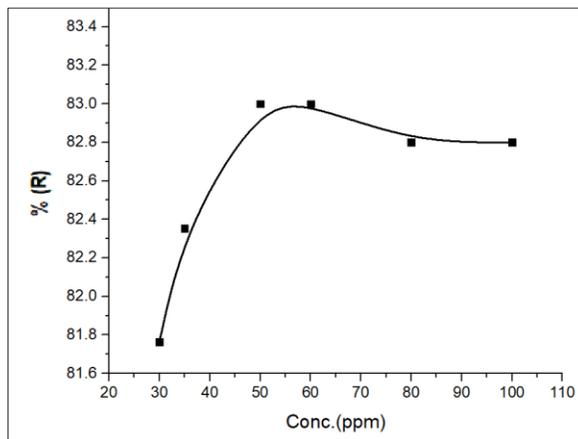
Figure 8. Effect of initial concentration of AMP drug

The Freundlich isotherm model, which is based on an assumption about energetic surface heterogeneity, is the earliest known relation defining nonideal and reversible adsorption that may be used for multilayer adsorption [28]. Equation 3 serves as a representation of the Freundlich isotherm model's non-linear expression [34]:

$$\log q_e = \log K_f + (1/n) \log C_e \qquad \text{Eq. 3}$$

Where K_F is the adsorption capacity (l/mg), and $1/n$ is the adsorption intensity, it also represents the relative energy distribution and the heterogeneity of the sites of adsorbate [34]. The adsorption parameters are summarized in Table 1. Based on the correlation value (R^2), the Freundlich model with $R^2 = 0.991$ describes the isotherm data better than the Langmuir model with $R^2 = 0.948$. Fig. 9 shows both Langmuir and Freundlich adsorption isotherm models.

Table 1. Adsorption parameters of Freundlich and Langmuir isotherms models.

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg/g)	b (l/mg)	R^2	K_f (l/mg)	n	R^2
1.129	0.069	0.948	5.920	0.381	0.991
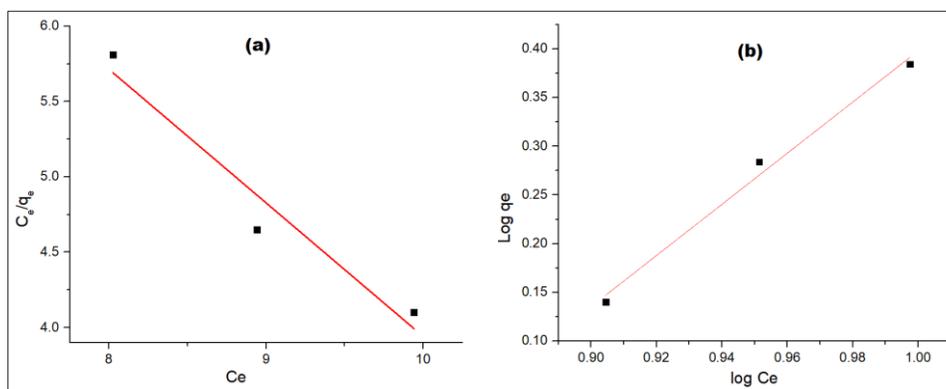
Figure 9. (a) Langmuir isotherm model, and (b) Freundlich isotherm model for the adsorption of AMP drug by SCO roots biosorbent

3.7. Kinetics Studies

The adsorption mechanism of the removal of AMP by the SCO biosorbent was studied using pseudo-first-order and pseudo-second-order kinetic models within time intervals between 15 to 120 min. The two kinetic models can be represented using equations 4 and 5, respectively [17,35]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \qquad \text{Eq. 4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{Eq. 5}$$

Where q_e and q_t are the amounts of adsorbed AMP per 1 g of SCO biosorbent (mg/g) at equilibrium and at time t, respectively. The k_1 (min^{-1}) and K_2 (g/mg min) are the rate constants for pseudo-first-order and pseudo-second-order reactions, respectively. The results are represented in Fig. 10. Based on the results shown in Table 2, the correlation coefficient (R^2) is relatively higher for the pseudo-second-order model than that of the pseudo-first-order one. This suggests that the adsorption of AMP on the SCO surface is a chemisorption process that might include electron exchange between the sorbent and adsorbate species [17,31].

Table 2. Pseudo-first-order and pseudo-second-order parameters for the adsorption of AMP on SCO.

Pseudo First-Order Kinetic Model			Pseudo Second-Order Kinetic Model		
q_e *(mg/g)*	k_1 *(min^{-1})*	R^2	q_e *(mg/g)*	k_2 *(g/mg.min^{-1})*	R^2
11.220	0.014	0.992	3.896	0.015	0.999
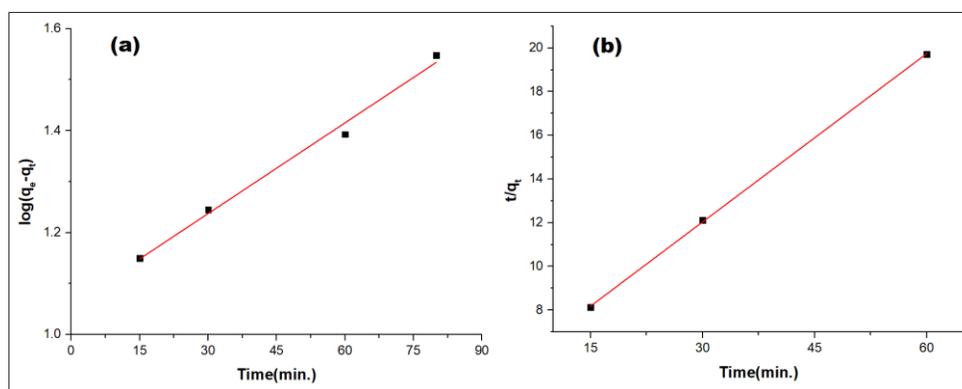
Figure 10. (a) pseudo-first-order and (b) pseudo-second-order kinetic models

3.8. Thermodynamics Studies

The thermodynamic model was studied to describe the nature and mechanism of the adsorption of AMP on SCO in aqueous media. The mixture was stirred magnetically at temperatures between 40 to 100°C [17,24]. The value of Gibbs free adsorption energy ($\Delta G°$), the enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were determined using equations 6, 7, and 8:

$$\Delta G° = -RT\ln K_c \qquad \text{Eq. 6}$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad \text{Eq. 7}$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad \text{Eq. 8}$$

Where R is the gas constant (8.315×10^{-3} kJ.mol^{-1}.K^{-1}), K_C (C_{ad}/C_e) refers to the adsorption distribution coefficient, C_{ad} (mg/l) is the amount of drug adsorbed on the sorbent at equilibrium, and T is the temperature in Kelvin. The values of ($\Delta H°$) and ($\Delta S°$) were determined from the slope of the linear plot of $\ln K_c$ vs. $1/T$, as shown in Fig. 11. The values of the thermodynamic parameters are represented in Table 3. The negative values of ($\Delta G°$) refer to the spontaneous nature of the adsorption process of AMP on SCO [30]. The negative value of ($\Delta H°$) indicates that the adsorption process is exothermic [30]. The positive value of ($\Delta S°$) shows the increase in randomness at the SCO surface during the adsorption of AMP [17].

Table 3. Thermodynamic parameters of the adsorption of AMP onto SCO roots from aqueous media.

Temperature (K)	K_c (C_{ad}/C_e)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/K/mol)
313	2.880	-102.645	-50.201	0.168
333	1.825	-105.996		
343	19.955	-107.672		
358	30.696	-110.185		
373	16.759	-112.698		
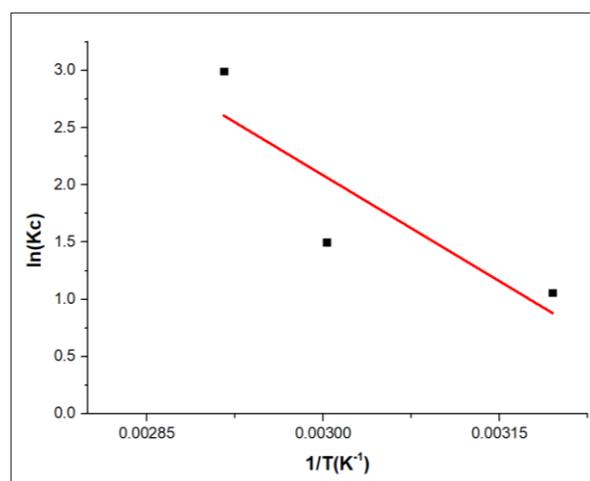
Figure 11. A Thermodynamic plot of *lnKc* against *1/T* for sorption of AMP from aqueous media

3.9. Comparison with other Biosorbents

A comparison between the efficiency of SCO and other biosorbents for removing AMP drugs from aqueous media is summarized in Table 4.

Table 4. Comparison of the removal efficiency of AMP by SCO and other bio-sorbent materials.

Biosorbent	Removal Efficiency	Reference
Chitosan bio-polymer	79%	Amr M. et al. [17]
Salvadora persica seeds ash	96%	Ho, Y. et al. [36]
Salvadora persica roots ash	98%	
Saussurea costus roots	83%	This work

4. Conclusion

The roots of the *Saussurea costus* (SCO) plant were used as a new biosorbent to remove Amprolium hydrochloride (AMP) veterinary antibacterial drug residues from aqueous media. The influence of different variables was investigated, including the initial concentration of the AMP drug, the solution's pH value, contact time, adsorbent dosage, and temperature. The results showed that the optimal removal of AMP was reached at a pH of 3.6 at 80 min contact time using a sorbent dosage of 0.04 g at a temperature of 45°C. The maximum removal percentage of AMP under optimal conditions was 83%. Adsorption isotherm study showed that AMP adsorption correlates more strongly to the Freundlich isotherm model with $R^2 = 0.991$. The kinetics studies showed that the adsorption follows a pseudo-second-order model with $R^2 = 0.999$, suggesting it is a chemisorption process. The values of thermodynamic parameters indicate that the adsorption process of AMP on SCO is spontaneous and exothermic, with an increase in randomness during the adsorption. From the results, the SCO plant roots can be used as an eco-friendly adsorbent for efficiently

removing AMP drugs from aqueous media. However, the main challenge with bio-adsorptive removal techniques is that they may not be as cost-effective in more extensive urban and industrial applications as in small-scale applications. Therefore, the economic factor shall be considered before adopting a specific bio-adsorptive technique for a particular application.

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