

## Heavy metals biosorption by *Thapsia transtagana* stems powder: Kinetics, equilibrium and thermodynamics

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### Abstract

The present study investigates the biosorption potential of natural and low-cost biosorbent *Thapsia transtagana* stems (TTS) form for the removal of cadmium (II) and cobalt (II) ions from aqueous solution. The surface of TTS has been thoroughly characterized by FTIR spectroscopy, scanning electron microscopy–energy-dispersive X-ray spectroscopy, Boehm titration, and point of zero charge. Batch biosorption experiments were carried out to evaluate the effect of process parameters, viz solution pH, biosorbent dosage, contact time, initial metal ion concentration and temperature on the biosorption of Cd(II) and Co(II) ions using the biosorbent. Experimental results show that, the biosorption process is very rapid and the biosorption yield increases with an increase in biosorbent dosage. Maximum biosorption was occurred at pH between 6 and 7. Kinetic data were properly fitted with the pseudo-first-order model instead of pseudo-second-order model. Biosorption isotherms were best correlated with Langmuir model than with Freundlich model. The biosorption of the metals ions was exothermic in nature ( $\Delta H^\circ = -20.10$  kJ/mol for Cd(II) and  $-20.87$  kJ/mol for Co(II)). When the temperature was increased from 25°C to 55 °C, the reaction was accompanied by a decrease in entropy ( $\Delta S^\circ = -73.42$  J/K.mol for Cd(II) and  $-84.38$  J/K.mol for Co(II)).

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## 1. Introduction

Water pollution caused by heavy metals is of critical concern due to its inherent nature of being persistent, toxic, recalcitrant and non-biodegradable. The bio-accumulating aspect of heavy metals threatens the food chain and human health ultimately [1]. The most commonly found heavy metals in wastewater include arsenic, cadmium, chromium, copper, lead, nickel, zinc, etc. Cadmium is a nonessential element for organisms and its high toxicity for humans has been recognized. Pollution by Cd(II) usually comes from several industrial processes such as electroplating, plastics manufacturing, nickel-cadmium batteries, fertilizers, pigments, mining and metallurgical processing. Cd(II) toxicity may be observed by a variety of syndromes and its effects include renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [2]. Cobalt is a naturally occurring element, a heavy metal, an essential micro-mineral that is required to orchestrate the normal physiological function of human body. However, higher concentration of cobalt has profound ill-effects resulting in contact dermatitis, paralysis, lung irritation and bone defects [3]. Cobalt is used in the manufacture of super alloys, lithium ion batteries, oxidation catalysts, and as pigments in paints [4]. These industries are susceptible to discharge high levels of cobalt contaminated effluents into the aquatic environment. Consequently, there is significant interest regarding Cd(II) and Co(II) removal from wastewaters. Several treatment methods can be used for efficient removal of heavy metals from aqueous solution, such as filtration, chemical precipitation, coagulation, solvent extraction, ion exchange, membrane process, bioremediation and adsorption [5,6]. Among these techniques, adsorption has been recognized as one of the most popular methods due to its simplicity of design, high efficiency, easy recovery and cost-effectiveness [7]. Recent progress in environmental technology encourages the use of biosorbents for the removal of toxic heavy metals from aqueous solutions [8]. Natural materials that are commonly used for the purpose are mung bean husk [9], xanthated nano banana cellulose [10], rapeseed waste [11], shell dust of *Lymnaea* [12], eggshell [13] and barley straw ash [14]. The objective of this work is to investigate the applicability of plentiful, easily available and nontoxic plant; *Thapsia transtagana* stems as eco-friendly biosorbent for the removal of cadmium(II) and cobalt(II) ions from aqueous solution. Studies were carried out under various parameters such as solution pH, biosorbent dosage, contact time, initial metal ions concentration and temperature. Biosorption kinetic data were tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich models. The surface properties of biomass were characterized by FTIR spectroscopy, scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDX), and the pH of point of zero charge (pHpzc). The functional groups were also determined by Boehm titration.

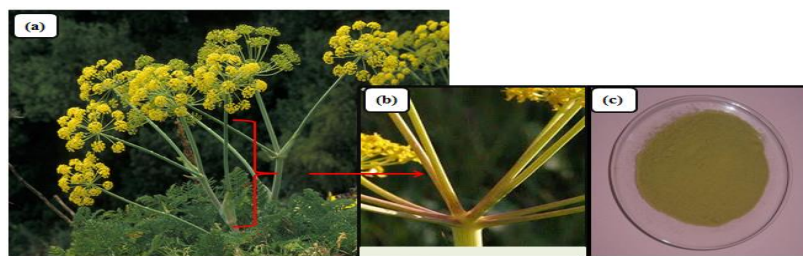
## 2. EXPERIMENTAL

### 2.1 Materials

All chemicals such as Cd (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (98%), Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%), NaCl (99.5%), HCl (37%), Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> were obtained from Sigma-Aldrich (Germany). HNO<sub>3</sub> (65%) from Scharlau (Spain) and NaOH (98%) was provided from Merck (Germany).

### 2.2. Preparation of the biosorbent

*Thapsia transtagana* (TT) Fig.1(a) used in this study was collected from the region of Oued zem in Morocco. The *Thapsia transtagana* stems Fig. 1(b) was first cleaned, dried in sunlight and then cut into small pieces. The cutted materials were then powdered to a particle sizes < 125 µm using a domestic mixer. The powder Fig.1(c) of biosorbent was stored in hermetic glass bottles.



**Fig. 1:** Plant of *Thapsiatranstagana*(a), *Thapsiatranstagana* stems (b) and powder of *Thapsiatranstagana* stems (c).

### 2.3. Characterization

FTIR transmittance spectra of the biosorbent were recorded in the region of 4000–400  $\text{cm}^{-1}$  by using a Scottech-SP-1 spectrophotometer. Scanning electron microscopy (SEM) was used to study the morphology of TTS by using a FEI Quanta 200 model. The pH of point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of biosorbent is an important characteristic that determined by Noh and Schwarz. [15]. In this method, 50 mL of 0.01 mol/L NaCl solution was poured into six different beakers and pH of those solutions were adjusted to pH 2, 4, 6, 8, 10, and 12 by adding  $\text{HNO}_3$  and NaOH, where necessary. Around 0.05 g of biosorbent was added to each of beakers and all the beakers were agitated for 6 h. Afterward, the liquids were filtered and the final pH of the solution were measured. The final pH was plotted vs. the initial pH. A tie line was drawn, where initial pH was equal to final pH. The intersecting point between those two lines was identified as  $\text{pH}_{\text{PZC}}$ . Basic and oxygenated acidic surface groups were quantified by Boehm titrations [16]. A known amount of biosorbent (about 0.1 g) was added into a 50 mL of 0.01 M each of the three bases and one acid i.e., NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and HCl. The mixtures were stirred at 500 rpm for 24 h at room temperature. The solution was then filtered using a membrane filter (0.2  $\mu\text{m}$ ) to remove the biomass from the solution. To determine the oxygenated groups content, back titrations of the filtrate (10 mL) were achieved with standard 0.01 M HCl solution. Basic groups contents were also determined by back titration of the filtrate with 0.01 M NaOH solution.

### 2.4. Batch biosorption experiments

The stock solutions of cadmium and cobalt (1000 mg/L) for the experimental purpose was prepared by dissolving required amounts of Cadmium nitrate tetrahydrate and Cobalt nitrate hexahydrate separate in deionized water and diluted further to get different concentrations of working solutions. The biosorption experiments were conducted to determine the efficiency of TTS for the elimination of Cd(II) and Co(II) from aqueous solution under various process conditions. The pH of the initial solution was analyzed over the pH range 2–7 at an initial metal concentration of 100 mg/L by adding 0.1 N NaOH and/or 0.1 N  $\text{HNO}_3$  solutions. The biosorbent dosage was varied from 0.5 to 6 g/L. The contact time was carried between 2 and 180 min at room temperature with initial pH solution. Biosorption equilibrium was established for different metal ion concentration between 20 and 200 mg/L. The effect of temperature was tested in the range of 25 to 55  $^{\circ}\text{C}$  using a thermostatically controlled incubator. After each biosorption experiment was completed, the biomass was separated from the liquid phase by centrifugation at 3,000 rpm for 10 min. Samples were diluted by distilled water, and the residual concentrations were analyzed by Atomic Absorption Spectrophotometer (AAnalyst 200). The biosorption capacity and biosorption removal efficiency were calculated using the following equations:

$$q = \frac{C_0 - C}{R} \quad (1)$$

$$\% \text{ Removal} = \frac{C_0 - C}{C_0} * 100 \quad (2)$$

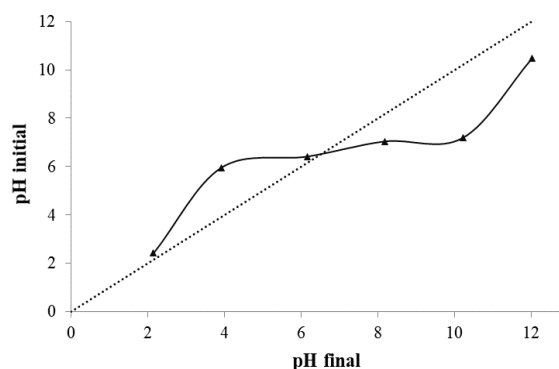
where  $q$  is the adsorbed amounts (mg/g),  $C_0$  is the initial dye concentration (mg/L),  $C$  is the dye concentration after biosorption, and  $R$  is the mass of biosorbent per liter of solution (g/L). Kinetic and equilibrium parameters were estimated with the aid of the non-linear regression using Origin 6.0 software.

### 3. RESULTS AND DISCUSSION

#### 3.1. Boehm titration and pH of zero charge

Surface functional groups play an important role in sorption processes. These functional groups are principally divided as acidic or basic groups, which affect the surface charge of the biosorbent and consequently the biosorption efficiency [17]. Boehm titration was applied for raw material TTS to quantify acidic functional groups, the results are shown in Table 2. according to the results obtained it can be seen that the *Thapsia transtagana* stems surface are constituted mainly of acidic groups which are due to presence of carboxylic, phenolic, and lactonic groups and a less quantity of basic groups. Generally, biosorbent with greater surface acid groups have a higher cation exchange property. These results suggest greater sorption performance of TTS for metal ions. The pH<sub>pzc</sub> of the biosorbent was found to be 6.5 (Fig. 3). This value is in agreement with Boehm titration result, which shows a dominance of acidic groups at the surface of the biosorbents.

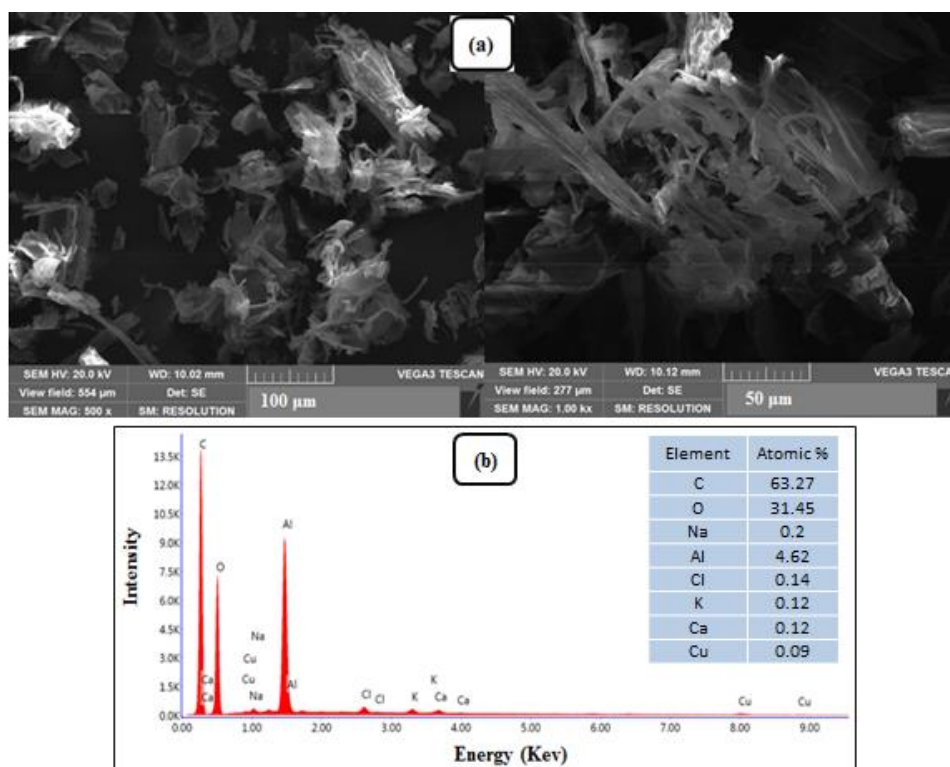
Carboxylic	Lactonic	Phenolic	Total acid	Total basic
0.484	0.494	0.516	1.494	0.409



**Fig.3:** Determination of the point of zero charge (pHpzc) of TTS.

#### 3.2. SEM-EDX analysis

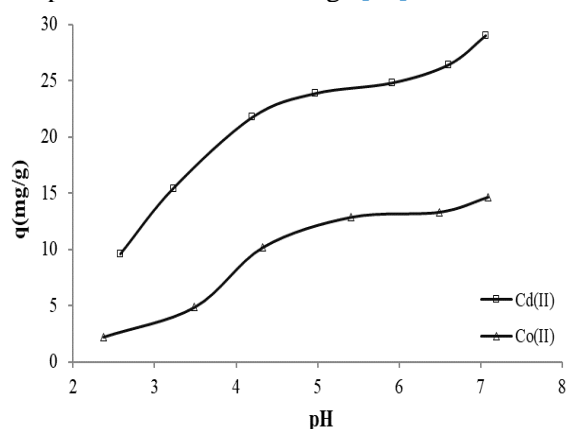
The scanning electron micrograph (SEM) of TTS is shown in Fig. 4a. As shown in Fig. 4a the TTS has rough surface with irregular structure morphology and pores of different size and different shape. This kind of morphology can promote the biosorption of metals ions on different parts of the biosorbent. The chemical composition was identified by the Energy Dispersive X-ray analysis. The EDX spectrum with chemical compositions for TTS is given in Fig. 4b. The EDX spectrum revealed mainly the presence of carbon (63.27%) and oxygen (31.45%) associated with some minerals such as potassium, calcium and sodium.



**Fig.4:** SEM images and EDX analysis of TTS

### 3.3.Effect of solution pH

As one of the critical parameters in the biosorption, pH of the metal ion solution could affect the surface charge of the biosorption and the metal ion chemistry. Also, the biosorbents surface has a variety of functional groups, such as carboxyl, hydroxyl and amine. These groups are involved in almost all potential binding mechanisms. Moreover, the affinity of ionic species toward the functional groups present in the cellular surface is strongly affected by pH value, in same as these functional groups participate in metal ion bindings [18].



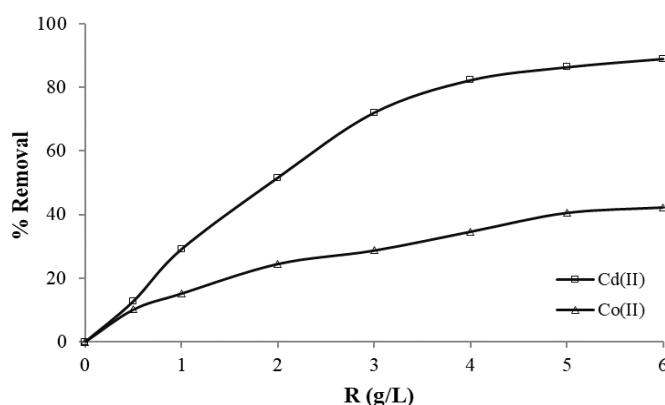
**Fig.5:** Effect of pH on the biosorption of Cd (II) and Co (II) onto TTS:  $C_0 = 100$  mg/L, contact time = 120 min,  $R = 2$  g/L,  $T = 25$  °C.

For that, we investigated the influence of pH was performed by varying the pH from 2 to 7 for Cd(II) and Co(II) the results were shown in Fig.5. It can be seen that, the biosorption of the two metals was low in acidic medium and increase with increasing the solution pH. In general, the biosorption of metals increases with increasing pH. The pH of zero charge ( $pH_{PZC}$ ) of the biosorbent was found to be 6.59. At pH values above this points, the biosorbent surface

become negatively charged and positively charged for underneath values [19]. Consequently the ionic sorbent–sorbate interaction becomes progressively significant for pH higher than 6.59. The enhancement in metals removal for pH beyond 7 can be affected the participation of precipitation of metals at these conditions.

### 3.4. Effect of biosorbent dosage

The biomass dosage is an important parameter as it determines the capacity of a biosorbent for a given initial concentration [20]. The Cd(II) and Co(II) ions uptake on TTS was studied using different biosorbent dosages of 0.5, 1, 2, 3, 4 and 6 g/L in 100 mg/L initial metal ion concentration solution and at initial pH. Fig. 6 represents the effect of biosorbent dosage on Cd(II) and Co(II) removal. As shown in this figure there was an increase in sorption capacity whenever there was an increase in biomass dosage from 0.5 to 6 g/L. Also, the biosorption yield of metal ion increased from 12.77 to 94.98 % and from 10.14 to 50.82 % respectively for Cd(II) and Co(II) when the biosorbent dosage was increased from 0.5 to 6 g/L. This can be expected because the higher dose of biosorbent in the solution, the greater availability of exchangeable sites for the metals ions [21].



**Fig.6:** Effect of biosorbent dosage on the removal of Cd(II) and Co(II) onto TTS:  $C_0 = 100$  mg/L, contact time = 120 min, initial pH,  $T = 25^\circ\text{C}$ .

### 3.5. Biosorption kinetics

Studies on the kinetics of the process of Cd(II) and Co(II) removal by TTS at room temperature and up to 180 min was studied using solutions containing 100 mg/L concentration of metal ions at initial pH out with the purpose of observing the progress of the process up to the time that system reached equilibrium. It can be deduced from Fig.7 that the biosorption process comprised of two phases: a primary rapid removal step at 30 min and a second one exhibit a subsequent removal until equilibrium is reached, which is slow and quantitatively insignificant step. Since there is no significant increase on Cd(II) and Co(II) sorption after 120 min, the equilibrium could be considered to be taking place at 120 min to ensure the optimum sorption. Biosorption kinetics data were analyzed using two kinetic models, pseudo-first-order model [22] and pseudo-second-order model [23]. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows:

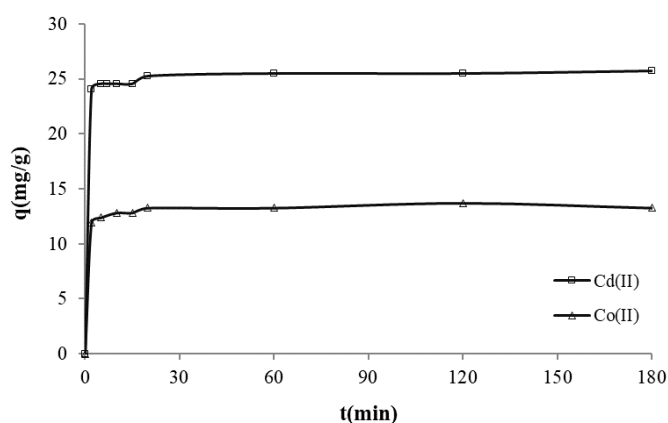
$$q = q_e(1 - e^{-K_1 t}) \quad (3)$$

where  $q_e$  and  $q$  (both in mg/g) are, respectively, the amounts of dye biosorbed at equilibrium and at any time  $t$  (min) and  $k_1$  (1/min) is the rate constant of biosorption. The pseudo-second-order model can be expressed as:

$$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (4)$$



where  $k_2$  (g/mg min) is the rate constant of pseudo second-order biosorption. Parameters of the pseudo-first-order and pseudo-second-order models were estimated with the aid of the non-linear regression. The obtained data and the correlation coefficients  $r^2$  are given in Table 3. As seen from this table, the calculated equilibrium values ( $q_{cal}$ ) from pseudo-first-order model were close to the experimental values ( $q_{exp}$ ) than the others calculated from the pseudo-second-order kinetic model. Moreover, the correlation coefficients were closer to 1 in the case of pseudo-first-order than of pseudo-second-order model. This result suggests that the biosorption of Cd(II) and Co(II) onto TTS could be better described by the pseudo-first-order model instead of pseudo-second-order kinetic model.



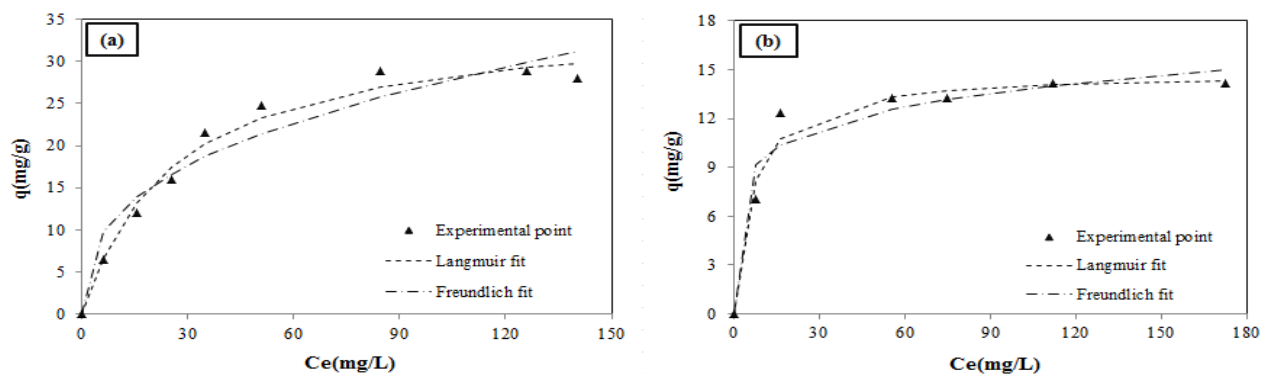
**Fig.7:** Kinetics of Cd(II) and Co(II) biosorption by TTS:  $C_0 = 100$  mg/L,  $R = 2$  g/L, initial pH,  $T = 25$  °C.

**Table 3:** Pseudo-first-order and pseudo-second-order kinetic parameters for the biosorption of Cd(II) and Co(II) by TTS.

Metal	$q_{exp}(mg/g)$	Pseudo first-order			Pseudo second-order		
		$q_{cal} (mg/g)$	$k(1/min)$	$r^2$	$q_{cal} (mg/g)$	$k(g/mg \text{ min})$	$r^2$
Cd(II)	25.469	25.340	0.323	0.999	25.052	1.613	0.998
Co(II)	13.717	13.329	1.197	0.993	13.093	0.282	0.985

### 3.6. Biosorption isotherms

Biosorption isotherm is useful in finding out the adsorption capacity of the biosorbent, the distribution of the solute between the liquid and solid phases at various equilibrium concentrations and the degree of accumulation of adsorbate on the surface of the biosorbent [24].



**Fig. 8:** Adsorption isotherms of Cd(II) (a) and Co(II) (b) onto TTS.

The data under the study of biosorption isotherm are to be specific for each system and the determination of isotherm data are to be carried out for every application. The biosorption isotherms are given in Fig. 8. The figure indicates that metal ions removal is highly concentration dependent. It is clear that the amount of metal biosorbed increases as its equilibrium concentration increased. From these data, biosorption isotherms of metal ions were steep, indicating a greater affinity of metal ions on the biosorbent. The equilibrium biosorption data were analyzed with both the Langmuir [25] and the Freundlich isotherms [26].

### 3.7 Langmuir model

The Langmuir isotherm (1916) assumes that the numbers of surface biosorption sites are fixed, biosorption behavior is independent of surface coverage and all adsorption sites are represented by similar types of functional groups. The Langmuir model is the most frequently used in many sorption processes to evaluate the maximum sorption capacity. The linear form of Langmuir isotherm is represented as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where  $q_m$  (mg/g) is the maximum monolayer biosorption capacity and  $K_L$  (L/mg) is the Langmuir equilibrium constant related to the biosorption affinity.  $C_e$  is the equilibrium concentration.

### 3.8. Freundlich model

The Freundlich isotherm is an empirical model of heterogeneous surface sorption with non-uniform distribution of heat sorption and affinities. The form of the Freundlich equation can be stated as follows:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where  $K_F$  ( $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ ) is the Freundlich constant and  $n$  is the heterogeneity factor. The  $K_F$  value is related to the biosorption capacity; while  $1/n$  value is related to the biosorption intensity.

**Table 4:** Isotherm constant parameters and correlation coefficients calculated for the biosorption of Cd(II) and Co(II) onto TTS.

Metal	Langmuir			Freundlich		
	$q_m$ (mg/g)	$K_L$ (L/mg)	$r^2$	$K_F$ ( $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ )	$n$	$r^2$
Cd(II)	35.35	0.038	0.984	5.09	2.73	0.938
Co(II)	14.84	0.162	0.976	6.68	6.35	0.942

Biosorption isotherm parameters of Langmuir and Freundlich models for the biosorption of Cd(II) and Co(II) onto TTS are summarized in Table 4. From the table, it can be seen that Langmuir model indicates higher values of correlation coefficients than Freundlich model. These results indicated that the biosorption of metals was best fitted by the Langmuir isotherm model. The maximum monolayer biosorption capacities were found to be 35.35 and 14.84 mg/g, respectively for Cd(II) and Co(II). It is important to compare the adsorption capacity of TTS with other biosorbents. This comparison suggests the effectiveness of TTS in removing of Cd(II) and Co(II) from aqueous solution. The adsorption capacity values of different biosorbents reported in previous literatures are presented in Table 5. As it can be seen, maximum biosorption capacity obtained in the present study was either of the same order or higher than the other reported biosorbents at a very low biosorbent dose.



**Table 5:** Comparison of biosorption capacity of TTS for Cd(II) and Co(II) with different related biosorbents.

Biosorbent	qm (mg/g) Cd(II)	qm (mg/g) Co(II)	References
Glebioniscoronaria L.	25.24	33.02	[27]
Diplotaxisharra	18.31	24.52	[27]
Raw-carb	31.35	17.41	[28]
Apple peels	0.80	–	[29]
Mandarin peels	3.33	–	[29]
Spirogyra hyaline	18.18	12.82	[30]
Natural hemp fibre	–	13.58	[31]
Watermelonrind	–	23.30	[32]
Lemonpeel	–	22.00	[33]
Banana peels	5.91	–	[34]
C. indicum flowers	–	14.84	[35]
Latesniloticus fish bones	–	17.89	[36]
mangosteen shell	3.15	0.34	[37]
Sawdust	21.3	–	[38]
Sunflower plant	35.97	–	[39]
Brown seaweed	–	0.63	[40]
Husk of Lentil	29.41	–	[41]
<i>Thapsia transtagana</i> stems	35.35	14.84	This study

### 3.9. Effect of temperature and thermodynamic parameters

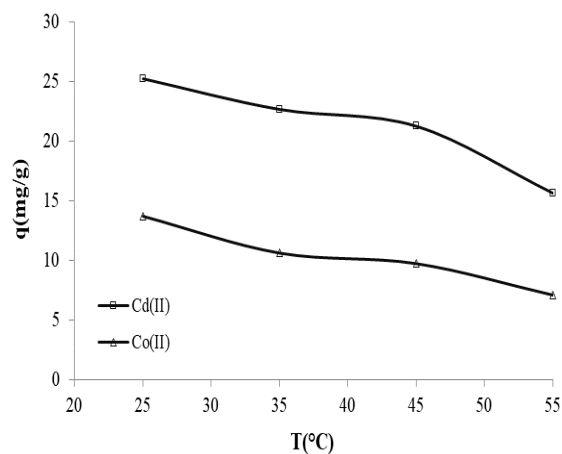
Temperature is an important parameter in the biosorption processes and its effect was studied in the temperature range 25–55 °C as shown in Fig.9. This figure indicates that temperature have significant influence on the biosorption capacity in the studied range. A decrease in the removal efficiency was observed with an increase in solution temperature. Generally, the temperature has two major effects on the biosorption process. Increasing the temperature is known to increase the rate of the diffusion of molecules across the external boundary layer and the internal pores of the biosorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the biosorbent for a particular adsorbate [42]. From these results, thermodynamics parameters such as enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ), and Gibb's free energy ( $\Delta G^\circ$ ) for the sorption have been calculated and presented in Table 6. Both the equilibrium constant  $K_D$  and  $\Delta G^\circ$  were determined using the following equations:

$$K_D = \frac{q_e}{C_e} \quad (7)$$

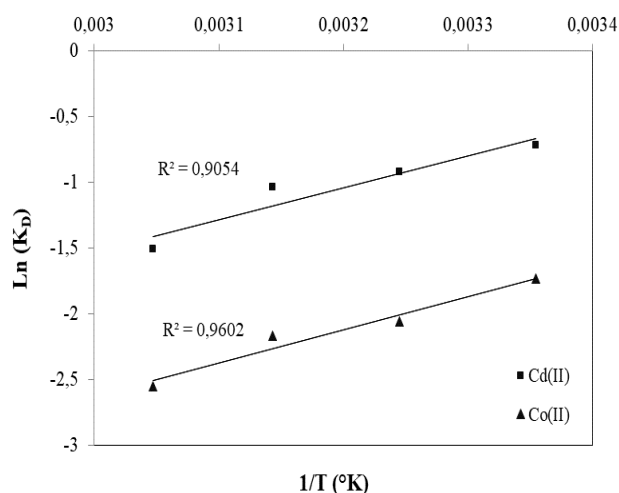
$$\Delta G^\circ = -RT \ln(K_D) \quad (8)$$

where R is the universal gas constant (8.314 J/mol K) and T is solution temperature in K. The enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of adsorption were estimated from the slope and intercept of the plot of  $\ln K_D$  versus  $1/T$  yields, respectively.

$$\ln(K_D) = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$



**Fig.9:** Effect of temperature on the biosorption of Cd(II) and Co(II) onto TTS:  $C_0 = 100$  mg/L, contact time = 120 min, initial pH,  $R = 2$  g/L.



**Fig.10:** Plot for  $(\ln K_D)$  versus  $(1/T)$ , gives a linear plot with a negative slope  $\Delta H$  and the intercept is  $\Delta S$ .

**Table 6:** Thermodynamic parameters calculated for the biosorption of Cd(II) and Co(II) by TTS.

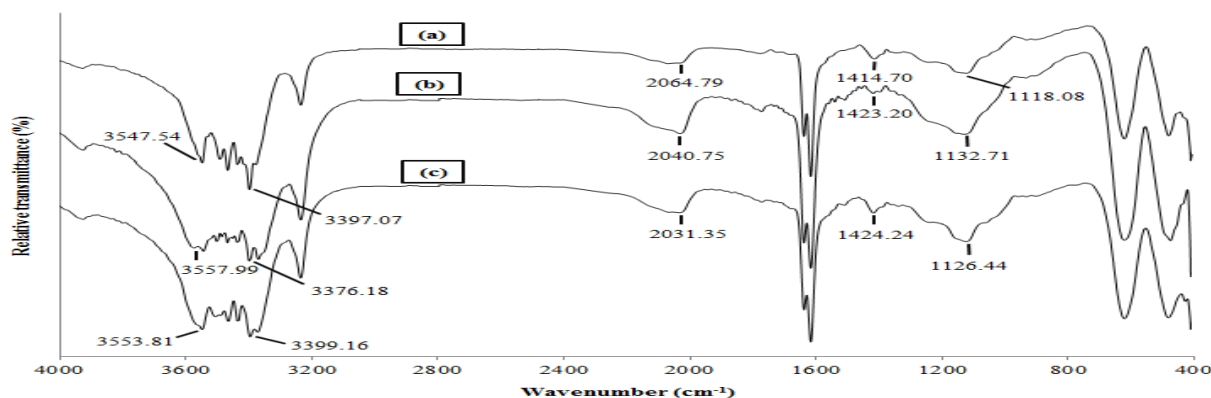
Metal	T	$K_D$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$
	(K)		(kJ/mol)	(kJ/mol)	(J/K.mol)
Cd(II)	298	0.487	1.79	-20.10	-73.42
	308	0.398	2.36		
	318	0.356	2.75		
	328	0.221	4.12		
Co(II)	298	0.178	4.29	-20.87	-84.38
	308	0.127	5.28		
	318	0.114	5.74		
	328	0.078	6.96		

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  have been taken from the slope ( $\Delta H^\circ/R$ ) and intercept ( $\Delta S^\circ/R$ ) of the plot  $\ln K_D$  vs  $1/T$ , which should give a straight line with acceptable coefficient of determination for Cd(II) ( $R^2 = 0.9054$ ) and Co(II) ( $R^2 = 0.9602$ ), Fig. 10. The positive values of  $\Delta G^\circ$  suggest that biosorption reaction requires energy for the biosorption of the ions metallic onto TTS. The increase in  $\Delta G^\circ$  values with increase in temperature shows a decrease in feasibility of

biosorption at higher temperatures. The enthalpy of biosorption ( $\Delta H^\circ$ ) was found to be -20.10 kJ/mol for Cd(II) and -20.87 kJ/mol for Co(II). The negative  $\Delta H^\circ$  is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. The negative value of  $\Delta S^\circ$  for the corresponding temperature interval indicated decreased randomness at the solid–solution interface with the loading of species onto the surface of TTS. It also suggested the probability of a favorable biosorption process.

### 3.10. Contribution of functional groups in the biosorption

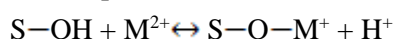
Direct information on the presence of surface functional groups can be obtained from FTIR studies. The spectrum of *Thapsia transtagana* stems presented in Fig. 2(a) categorizes different functional groups [43]. The broad strong and superimposed bands around 3,600–3,200  $\text{cm}^{-1}$  which may be due to overlapping of the stretching vibration of hydrogen-bonded of the hydroxyl group linked in cellulose, lignin, adsorbed water, and N–H stretching [44]. A weak absorption peaks at 1,757  $\text{cm}^{-1}$  is attributed to stretching of carboxyl groups. The band at 1,635  $\text{cm}^{-1}$  is indicative of OH bending vibrations. The strong absorption band at 1,614  $\text{cm}^{-1}$  is characteristic of C=O stretching vibrations of ketones, aldehydes, lactones, or carboxyl groups [28]. The band at 1,414  $\text{cm}^{-1}$  is corresponding of C–O stretching. The band at 1,360  $\text{cm}^{-1}$  assigned to C–N groups on the biomass surface. The absorption peaks around 1,160 and 1,060  $\text{cm}^{-1}$  are indicative of P=O and P–OH stretching vibrations. Peaks in the region of wavenumbers lower than 800  $\text{cm}^{-1}$  could be attributed to N-containing bioligands. To determine the functional groups involved in biosorption of Cd(II) and Co(II) onto TTS, a comparison between the FTIR spectra before (Fig.2a) and after biosorption of cadmium (Fig. 2b) and cobalt (Fig.2c) is carried out. The FTIR spectra confirmed changes in functional groups and surface properties of the biosorbent, illustrated by the shift of some functional groups bands due to Cd(II) and Co(II) biosorption (Table 1). These shifts may be attributed to the changes in counter ions associated with carboxyl and hydroxyl anions, suggesting that acidic groups, carboxyl and hydroxyl, are responsible of the biosorption of Cd(II) and Co(II) ions from aqueous solution.



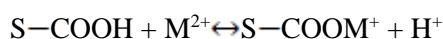
**Fig. 2:** FT-IR spectra of TTS (a), Cd loaded TTS (b) and Co loaded TTS (c).

From the Fourier Transformed Infrared and Boehm titration studies of *Thapsia transtagana* stems biosorbent, it can be seen that the acidic groups were more than the basic and may have been basically responsible for the biosorption of Cd(II) and Co(II) onto TTS biosorbent in the following manner:

For the phenolics it is



For carboxylic acid



The lone pair of electrons on the Lactone and amide present in the biosorbent may have been involved in the adsorption of metal ions from aqueous solution [45].

**Table 1:** FTIR spectral characteristics of TTS before and after biosorption of Cd(II) and Co(II) ions.

TTS	Wave number (cm <sup>-1</sup> )		Assignment
	Cd-TTS	Co-TTS	
3546.55	3547.6	3548.85	$\nu$ (O—H)
			$\nu$ (N—H)
2069.25	2031.55	2031.76	$\nu$ (C=C)
1615.95	1615.49	1615.85	$\nu$ (C=O)
1415.27	1417.33	1416.95	$\delta$ (O—H)
932.01	933.01	931.67	$\nu$ (=C—O—C)
			$\nu$ (P=O)
620.75	621.24	621.46	$\nu$ (P—OOH)
			$\delta$ (P—O—C)

$\nu$ : Stretching;  $\delta$ : bending (in-plane);  $\delta$ : bending (out-of-plane).

#### 4. CONCLUSION

Due to their low cost, good uptake capacity and short equilibration time, the local abundant plant (*Thapsia transtagana* stems) studied in this work are promising biosorbent materials for the removal of cadmium and cobalt from aqueous solutions. The batch study parameters; pH of solution, biosorbent dosage, contact time, temperature and initial Cd(II) and Co(II) concentrations were found to be important parameters on the biosorption processes. The experimental results show that the process is very rapid and the biosorption yield increased with an increase in the biosorbent dosage. Maximum biosorption was occurred at neutral pH. Kinetic data were tested using pseudo-first-order and pseudo-second-order kinetic models. The best fit was obtained with the pseudo-first-order kinetic model. Metal uptake increased with the increase in the initial concentration. Equilibrium data were correlated to Langmuir and Freundlich. Biosorption isotherms for metal ions were best fitted with Langmuir model. The negative value of  $\Delta H^\circ$  indicated that the biosorption process is exothermic.

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