

Kinetic and thermodynamic study for the removal of cadmium(II) ions from aqueous media by *Aucoumea klaineana* sawdust

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ABSTRACT

In this study, the biosorption by *Aucoumea klaineana* sawdust (AS) of cadmium(II) ions, from aqueous media was investigated under various operating conditions in a batch process. The influence of operating conditions such as initial concentration, ionic strength, initial pH solution, temperature, biosorbent dose, and biosorbent particle size on cadmium(II) ions removal by biosorption on AS is discussed. It was found that the equilibrium time at initial concentrations from 25 to 150 mg/L, was from 10 to 30 min, respectively. Pseudo-first-order, pseudo-second-order and Elovich models were used to fit the experimental data. The obtained results indicate that the biosorption system obeyed a pseudo-second-order kinetics model ($r \geq 0.987$). In addition, thermodynamic parameters such as ΔG° , ΔH° , and ΔS° were calculated. The thermodynamic study of biosorption isotherm indicated that the biosorption of cadmium(II) ions is spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ > 0$) process.

Keywords: *Aucoumea klaineana* sawdust; Cadmium(II); Kinetic; Modeling; Thermodynamic

1. Introduction

Heavy metal contamination is today one of the most important threats to the environment due to the increasing industrialization. Untreated effluents may have an adverse impact on the environment. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [1]. Due to its acute toxicity, cadmium is a heavy metal with the greatest potential hazard to humans and the environment. Cadmium poses a serious threat to human health as it accumulates in the environment throughout the food chain. Besides, the industrial uses of cadmium are widespread and increasing in electroplating, paint pigments, plastics, alloy preparation, mining, ceramics, and silver-cadmium batteries [2]. Cadmium has received a great deal of attention because the ingestion of cadmium above its permissible

limit causes serious problems in the organism as cancer, muscular cramps, renal degradation, chronic pulmonary problems, and skeletal deformity [3,4]. The drinking water guideline recommended by the World Health Organization (WHO) and American Water Works Association (AWWA) is 5×10^{-3} mg Cd/L [4–6]. However, the recommendation by the Official Journal of the Algerian Democratic and Popular Republic (JORDP) and OMS is 3×10^{-3} mg Cd/L. Therefore, it is very important to remove these heavy metals as cadmium from water environment, in order to protect the environment and offer people a better quality of live [6]. In this approach, several scientific studies have shown that popular processes, like ion exchange, electrochemical precipitation, solvent extraction, evaporation, reverse osmosis, membrane separation, foam separation, and adsorption by activated carbon were available for decontamination of metals from wastewaters. Unfortunately, the utilization of such methods has several important disadvantages, such

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as incomplete removal of metal ions, poor selectivity; high costs mainly in developing countries, high energy consumption, generation of large amounts of waste sludge, etc. [7]. Consequently, there is a necessary need to develop an inventive process, which can remove heavy metals efficiently from aqueous solution.

Biosorption processes, involving the retention of metal ions or other pollutants on solid materials of biologic origin, generally called biosorbents [7]. Biosorption processes are considered effective and can be an alternative solution for the removal of heavy metal from the aqueous solution, due to their important advantages (mainly due to reduced costs, an almost complete recovery of the retained heavy metals from depleted biosorbents, the minimization of resulting sludge, simplicity in operation, and ease of adaptation on an industrial scale, etc.) [7,8].

Recently, applying the biosorption process for the toxic heavy metal removal has been explored by some researchers for research of original biosorbents. Biosorption occurs as a result of a combination of several mechanisms, including Van der Waals attraction, electrostatic attraction, complexation, ion exchange, covalent binding, adsorption, and microprecipitation [6,9].

A number of low-cost biosorbents (natural materials or industrial and agricultural wastes) have been studied in the literature for their aptitude to remove the cadmium(II) ions from aqueous solutions in the last years, such as, respectively, fiber of fruit lufa, *Typha angustifolia*, mustard waste biomass, kraft lignin, *Pinus halepensis* sawdust, jackfruit peel, mungbean husk, and *Raphanus sativus* peels [4,6,8,10–14].

The agro-industrial wastes generally contains a variety of organic compounds (lignin, cellulose, and hemicelluloses) and functional groups (hydroxyl, carbonyl, and amino) [14,15]. Recognize that organic compounds and functional groups have an affinity for metal ion complexation [14,16,17].

Aucoumea klaineana sawdust (AS) is an exotic wood from equatorial West Africa (Gabon). It is mainly used for making panels, ply wood, interior carpentry, and cigar boxes. *A. klaineana* sawdust has been used as an original low-cost adsorbent for the removal of mercury and Rhodamine B in our previous works [18,19]. So, the aim of the present study is to complete the characterization of *A. klaineana* sawdust which has not been studied in the previous works and is to evaluate the applicability of an agro-industrial waste “*A. klaineana* sawdust” as an original biosorbent for the removal of cadmium(II) ions from synthetic aqueous media in batch process. Batch experiments were performed to examine the effect of physico-chemical parameters, such as initial pH solution, initial metal ions concentration, ionic strength, temperature, biosorbent dose, and biosorbent particle size. The kinetics approach of biosorption was studied by applying Lagergren pseudo-first-order, pseudo-second-order, and Elovich models. Additionally, thermodynamic parameters such as ΔG° , ΔS° , and ΔH° were determined.

2. Materials and methods

2.1. Preparation and characterization of AS

A. klaineana sawdust (AS) was washed, dried, and sieved to desired mesh size (0.5–1.25 mm). Finally, the obtained

material was then dried in an air circulating oven at 70°C for 3 d and stored in desiccators until use. Principle characteristics of the AS were determined and the results are summarized in Table 1 [18,19]. The surface functional groups of the AS were determined by the Boehm method [19] and the zero point charge (pH_{zpc}) of the AS characteristics was done with the addition solid method [20]. The specific surface area (SSA) of AS was determined using an alternative method to the Brunauer–Emmett–Teller (BET) method [20–22]. Mineralogical study was conducted on powder samples with an X-ray diffractometer (XRD) employing $\text{CuK}\alpha$ radiation. Additionally, the investigation of surface morphology (3,000× magnification) of AS sample was observed by scanning electron microscopy (SEM).

2.2. Aqueous metal ions solutions (Biosorbate)

Cd(II) solutions were prepared by dissolving requisite amount of $3\text{Cd}(\text{SO}_4)\cdot 8\text{H}_2\text{O}$ in distilled water. All other reagents used were of analytical grade. The pH of the solution was adjusted using H_2SO_4 (0.1 N) and NaOH (0.1 N).

2.3. Biosorption kinetic studies

The effects of experimental parameters, initial metal ions concentration (25–150 mg L^{-1}), biosorbent dose (0.2–1.5 g/150 mL), pH (3.0–6.0), ionic strength (0–2 g de KCL/150 mL), temperature (25°C–45°C), and biosorbent particle size (0.18–1.5 mm) on the biosorption of Cd(II) were conducted in discontinuous mode. The stirring speed (ω) was kept constant at 250 rpm for a period which is sufficient to reach equilibrium. Samples of the mixture were withdrawn at suitable time intervals, filtered through a filter paper for separate the biosorbent, with the aid of a suction pump. The metal concentration in the filtrate was analyzed by complexometry with EDTA (ethylenediaminetetraacetic acid) “Titriplex III.” The amount of metal ion biosorbed (Cd(II)) on AS at time t , q_t (mg/g) was determined using Eq. (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of the metal ion at initial and at any time respectively, V (L) is the volume of the solution and W (g) is the mass of the used biosorbent.

3. Results and discussion

3.1. Characterization of AS

The pH_{zpc} and the traditional Bohem titration of AS were previous studies determinate [18]. For pH_{zpc} was calculated using the addition solid method and which was determined to be 5.64 (Table 1), and the results [19] for the traditional Bohem titration (Table 2) prove that several types of surface groups exist and the total acid groups were higher than the total basic groups.

The SSA is the accessible area of biosorbent surface per unit mass of material. As an alternative to the BET method [20,21], the SSA ($\text{m}^2 \text{g}^{-1}$) of the AS was determined using the following equation:

Table 1
Principal characteristics of AS (*Aucoumea Klaineana* sawdust)

Porosity (%)	77.20
Apparent specific gravity	0.29
Absolute specific gravity	1.27
Mean diameter, d_m (mm)	≤ 1.25
Point of zero charge (pH _{zpc})	5.64

Table 2
Concentration of acid and basic groups on AS surface [19]

Concentration groups	Value (mequiv/g)
Carboxylic	0.08
Lactonic	0.49
Phenolic	1.24
Carbonylic and quinonic	1.43
Acid	3.22
Basic	0.41
Total	3.65

$$SSA = \frac{q_m \times N_{AV} \times A}{MW \times 10^3} 10^{-20} \quad (2)$$

where q_m is the monolayer capacity from Langmuir model (70.42 mg/g has been calculated) at 25°C, N_{AV} is the Avogadro number (6.022×10^{23}) molecules (mol^{-1}), A is the molecular area of ion cadmium (m^2), which the molecular area of cadmium ion was taken as 8.46 \AA^2 and MW is the molecular weight of the cadmium ($112.41 \text{ g mol}^{-1}$). According to Eq. (2), the SSA of AS was found as $31.91 \text{ m}^2 \text{ g}^{-1}$. This method has been already used to determine the SSA in the sorption of different pollutants by some authors [6,20–25].

SEM is one of the most widely used surface diagnostic tools. The scanning electron micrograph (SEM) of AS sample at bar length equivalent to $20 \mu\text{m}$, working voltage 5 kV with $3,000\times$ magnification is shown in Fig. 1. SEM image reveals that the textural structure of surface AS has a layered surface with a great number of cracks, cavities, and porous cell wall (heterogeneous), and this structural characteristic offer large surface area leads to able surface physical biosorption of cadmium ions.

In addition, the composition of AS was analyzed by XRD, which showed no obvious diffraction peaks (figure not shown), indicating that the AS was X-ray amorphous.

3.2. Effect of operating conditions

3.2.1. Effect of solution initial pH

It is known that the pH of the solution is the main essential parameter affecting metal ion sorption. This is for the reason that hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent. The effect of initial pH of the solution was analyzed over a pH ranges from 3 to 6. This pH range was chosen in order to avoid metal solid hydroxide precipitation and so

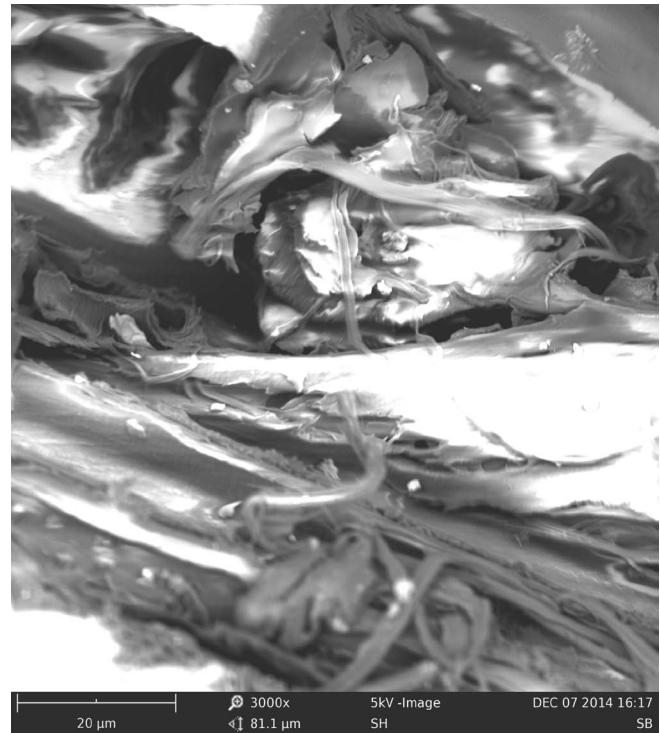


Fig. 1. SEM micrograph ($\times 3,000$) of *Aucoumea klaineana* sawdust (AS).

biosorption studies at these pH values could not be performed because the AS was deteriorated [4]. The pH of the solution was adjusted by either 0.1 N NaOH or 0.1 N H_2SO_4 solutions using a pH meter (ADWA AD1030 instruments). The pH of metal solutions is the major parameter controlling metal biosorption processes. This is because hydrogen ion competing with the positively charged metal ions on the active sites of the biosorbent. From Fig. 2, it was observed that the removal of cadmium biosorbed after equilibrium was from 9.75 at 31.54 mg g^{-1} , respectively, at initial solution pH was from 3.0 at 6.0. According to the cadmium speciation diagram, Cd^{2+} is the predominant ionic species at pH less than 7.0. So, cadmium was fixed on the AS as Cd^{2+} for all experiments carried [19]. The variation in the removal of cadmium by AS with respect to pH can be elucidated by considering the surface charge of the biosorbent materials and the speciation of cadmium ions. At lower pH values (3–4), the amount of removal of cadmium were found to be low due to the competitive biosorption of H^+ ions and ions for the same active surface sites [26]. At higher pH values (5–6), the amount of removal of cadmium was found to be high because the number of available positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favor the removal of positively ions metal due to electrostatic attraction. So, the optimum pH for the biosorption of cadmium(II) ions was 6.0. This value of initial pH has been reported for removal of cadmium by fruit luffa [4], *T. angustifolia* leaves [6], and eucalyptus bark [26]. While, all experiments in this study were carried out at natural pH (5).

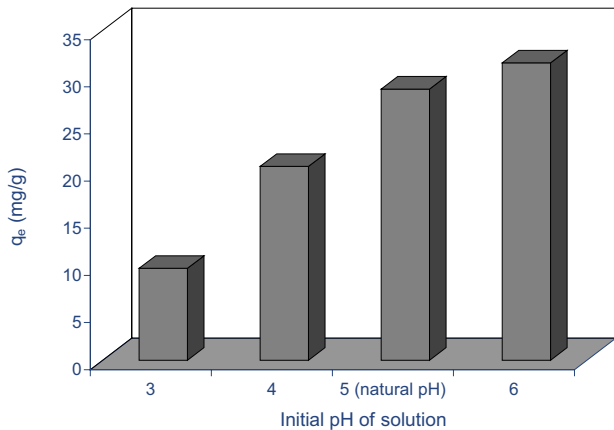


Fig. 2. Effect of initial pH on the biosorption of cadmium(II) ions by AS (conditions: C_0 : 100 mg/L; W : 0.2 g; ω : 250 rpm; initial pH: 3–6; T : 25°C).

3.2.2. Effect of initial concentration

The experiments were carried out at a fixed biosorbent dose (0.2 g), natural pH (5), stirring speed of 250 rpm, the constant temperature of 25°C was assured by a thermostatic water bath at different initial metal ion concentrations (from 25 to 150 mg/L) for different time intervals. The biosorption data for the uptake of cadmium vs. contact time at different initial concentrations are presented in Fig. 3. From this Fig. 3, for the different concentrations tested, it can be observed that the biosorption capacity increased with time (rapid in the initial stages) and reached a constant value where no more metal ions were removed from the solution, because there are a number of sites in AS constitution. As the cadmium/AS ratio increases, the active sites on AS surface are saturated, resulting in decreases in the biosorption efficiency. The initial rate of biosorption was better for higher initial cadmium ion concentrations, because the resistance to the cadmium ion uptake decreased as the mass transfer driving force increased. Equilibrium uptake increased with the increase of initial metal concentration at the range of experimental concentration. It was observed that the removal of cadmium biosorbed after equilibrium was from 7.18 to 40.07 mg g⁻¹, respectively, from 25 to 150 mg L⁻¹. Fig. 3 reveals that the biosorption of metal was a rapid process, which the contact time required to reach the equilibrium at initial concentrations from 25 to 150 mg/L, was from 10 to 30 min. This shows a good kinetic property of AS. However, in all experiments, the equilibrium time was maintained after 30 min, which was considered sufficient that full equilibrium was attained for the removal of metal ions on AS for higher concentrations.

3.2.3. Effect of ionic strength

The effect of ionic strength on the biosorption of metal ions on AS was studied with different concentrations of potassium chloride (0–2.0 g/150 mL). Fig. 4 shows that the biosorbed amount decreased with the increase in the concentration of salt (KCl) in the medium. This phenomenon can be explained as follows: the electrostatic attraction

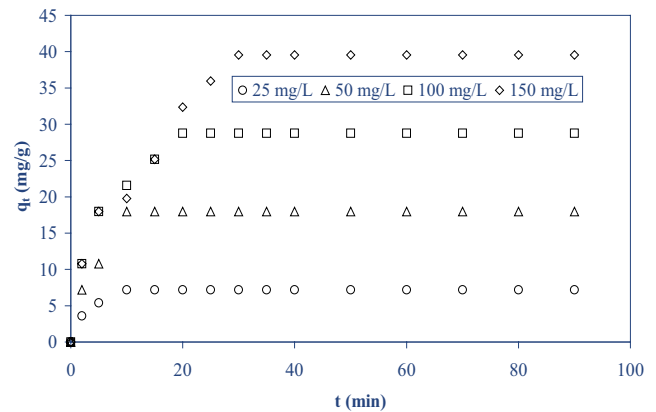


Fig. 3. Effect of initial concentrations and contact time on the biosorption of cadmium(II) ions by AS (conditions: C_0 : 25–150 mg/L; W : 0.2 g; ω : 250 rpm; initial pH: 5; T : 25°C).

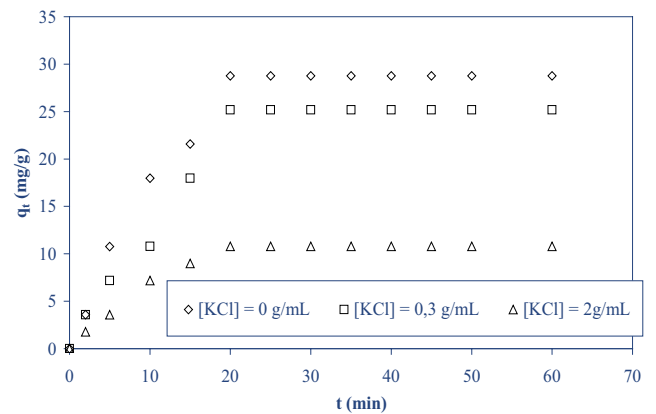


Fig. 4. Effect of ionic strength on the removal of cadmium(II) ions by AS vs. time (conditions: C_0 : 100 mg/L; W : 0.2 g; ω : 250 rpm; initial pH: 5; T : 25°C).

seems to be a significant mechanism, as indicated by the results, where at high ionic strength, the increased amount of KCl can help to render the surface of the AS not easily accessible to ions of cadmium and hence decreasing the biosorption rate [4].

3.2.4. Effect of temperature

Fig. 5 shows the evaluation of temperature for testing the aptitude of removal cadmium ions on AS. It was observed that the biosorption of cadmium increases with the increase in temperature from 25°C to 45°C. This indicates that the biosorption process of cadmium on AS is endothermic in nature. This phenomenon can be explained that the temperature provides the required energy for breaking down assured chemical barriers that could not have been otherwise broken [8,27], therefore the physical bonding between the cadmium ions and the active sites of the AS gets stronger. Also, as is known, the rate of diffusion of the sorbate ions is increased by increasing the temperature, owing to the decrease in the viscosity of the solution. This enhancement is felt to be due to the

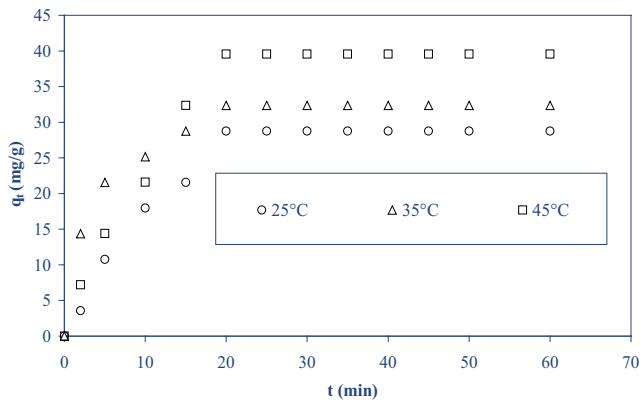


Fig. 5. Effect of temperature solution on the biosorption of cadmium(II) ions by AS vs. time (conditions: C_0 : 100 mg/L; W : 0.2 g; ω : 250 rpm; natural pH: 5; T : 25°C–45°C).

acceleration of the sorption process by the increased movement of metal ions from the bulk solution to the surface of the solid particles at higher temperatures [2]. Similar type of observation has been reported for *T. angustifolia* leaves [6], mustard waste [8], Kraft lignin [10], and wheat bran [2].

3.2.5. Effect of biosorbent dose

The biosorption studies of cadmium ions on AS were carried by varying biosorbent dosage from 0.2 to 1.5 g while keeping the temperature, stirring speed, initial metal ion concentration, and the volume of the metal solution constant at natural pH 5. Fig. 6 shows the effect of biosorbent dose on the biosorption of cadmium on AS, and it was observed that the biosorption capacity was lesser at higher biosorbent doses. This is due to greater availability of the exchangeable sites or surface area at a higher concentration of the biosorbent [28,29].

3.2.6. Effect of biosorbent particle size

The effect of biosorbent particle size on the cadmium ions removal was studied at different particle sizes. Fig. 7 shows the biosorption equilibrium of cadmium ions at three different particle sizes. It was observed that the removal is enhanced as the particle size decreases. This is because the smaller particles have more surface area and access to the particle pores is facilitated when their size is small. The amount of cadmium biosorption equilibrium decreases from 40.33 to 21.56 mg/g with an increase in particle size of AS from 0.18 to 1.5 mm, respectively.

3.3. Modeling of biosorption kinetics

The experimental results for different initial metal ions concentrations were modeled by the pseudo-first-order (Eq. (3)), the pseudo-second-order (Eq. (4)), and the Elovich (Eq. (5)) models [6,19]. The kinetic parameters were regrouped in Table 3.

$$\ln q_e - q_t = -K_1 t + \ln q_e \quad (3)$$

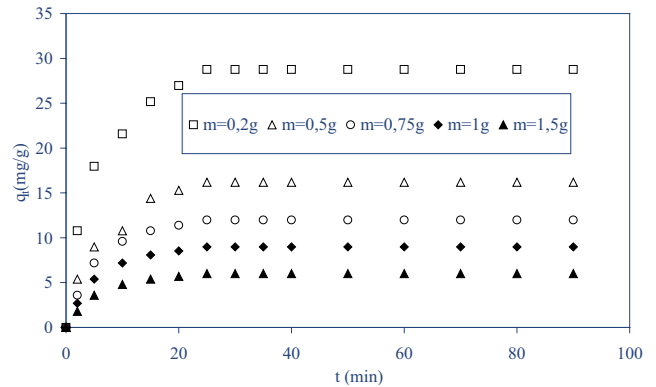


Fig. 6. Effect of biosorbent dosage on the removal of cadmium(II) ions by AS vs. time (conditions: C_0 : 100 mg/L; W : 0.2–1.5 g; ω : 250 rpm; natural pH: 5; T : 25°C).

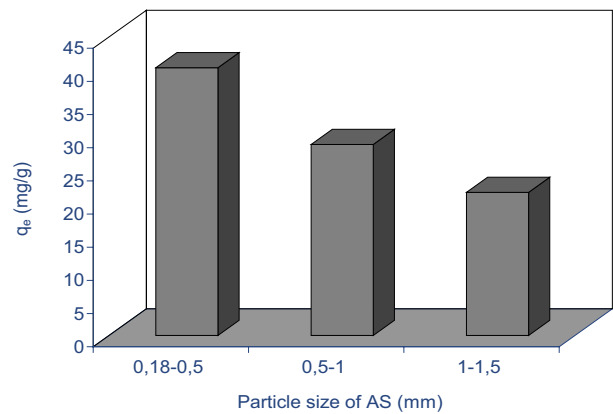


Fig. 7. Effect of biosorbent particle size on the biosorption of cadmium(II) ions by AS (conditions: C_0 : 100 mg/L; W : 0.2 g; ω : 250 rpm; natural pH: 5; T : 25°C).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

where q_e (mg/g) and q_t (mg/g) represent the biosorbed amount of metal ions at equilibrium and at any time t , respectively, and k_1 (min^{-1}) is the rate constant, k_2 (g/mg min) is the rate constant for the pseudo-first-order, the pseudo-second-order kinetics, α is the initial adsorption rate (mg/g min), and β is the desorption constant (g/mg).

The best-fit model was selected based on the magnitude of the regression correlation coefficient (r) as a first criterion, and the experimental amount biosorbed at equilibrium (q_e) will be close to the calculated amount biosorbed ($q_{e,cal}$) as a second one [6]. Table 3 illustrates the results for parameters of the kinetic models for the biosorption of cadmium on AS and as seen in this table that the linear regression correlation coefficient (r) values were found to be higher, (≥ 0.987) for pseudo-second-order model than for

Table 3
Parameters of the kinetic models for at different concentrations

Kinetics models	Initial concentration, C_0 (mg/L)			
	25	50	100	150
Pseudo-first-order				
$q_{e,exp}$ (mg/g)	7.18	17.97	28.78	40.07
$q_{e,cal}$ (mg/g)	31.48	12.85	95.98	39.87
k_1 (min^{-1})	0.055	0.063	0.092	0.074
r	0.872	0.939	0.918	0.890
Pseudo-second-order				
$q_{e,exp}$ (mg/g)	7.18	17.97	28.78	40.07
$q_{e,cal}$ (mg/g)	7.67	17.75	29.07	39.52
k_2 (g/mg min)	0.092	0.013	0.005	0.008
h (mg/g min)	0.45	0.79	0.78	1.43
r	0.999	0.987	0.997	0.998
Elovich				
α (mg/g min)	2.6	4.5	8.2	13.8
β (g/mg)	0.123	0.257	0.987	1.237
r	0.883	0.826	0.838	0.889

the pseudo-second-order and Elovich models and it was observed (Table 3) that the experimental ($q_{e,exp}$) values were agreed with the calculated ($q_{e,cal}$) values obtained from the linear plots for pseudo-second-order model. Consequently, these results indicate that the biosorption system at all initial concentrations obeyed the pseudo-second-order kinetics model.

The thermodynamic parameters that must be considered to determine the process as changes in enthalpy (ΔH°), entropy (ΔS°), and free energy (ΔG°) are calculated using the following equations [6,18]:

$$\ln b = \frac{\Delta S^\circ}{R_g} - \frac{\Delta H^\circ}{RT} \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

where (K) is the absolute temperature and R_g is the gas constant, and b (L/mol) is the Langmuir equilibrium constant. By using Eq. (6) the values of ΔH° and ΔS° of cadmium biosorption were determined from the slope and the

Table 4
Thermodynamic parameters for the biosorption of cadmium(II) ions by AS

T (K)	ΔH° (kJ/mol)	$-\Delta G^\circ$ (kJ/mol)	ΔS° (J/mol K)
298	11.39	11.56	77.04
308		10.73	71.84
318		10.65	69.31
328		10.55	66.90

intercept of the linear plot of $\ln b$ vs. $1/T$ (figure not shown). The Gibbs free energy change (ΔG°) was obtained according to Eq. (7). The calculated parameters by using the above equations were collected in Table 4. The negative values of ΔG° reveal the feasibility of the process and the spontaneous nature and the positive values of enthalpy change indicated the endothermic nature of the biosorption. Similarly, the thermodynamic parameters were reported for the removal of cadmium by mustard waste biomass [8].

4. Conclusion

The results of the present study showed that *A. klain- eana* sawdust can be a promising biosorbent for the removal of heavy metals such as cadmium(II) ions from aqueous media. The AS presents SSA of $31.91 \text{ m}^2 \text{ g}^{-1}$ and pH_{zpc} of 5.64. The concentrations of acid groups were higher than the basic groups and this result determines the nature of the AS surface which improves the biosorption of the cationic metal ion (cadmium(II)) from the media. SEM image ($\times 3,000$) of surface AS reveals that has a layered surface with a great number of cracks and cavities and the analyzed by XRD, indicating that the AS was amorphous.

The optimum pH for biosorption was 6.0. The amount of cadmium biosorbed was found to increase with an increase in the contact time, initial dye concentrations, pH, and the temperature. The contact time required to reach the equilibrium at initial concentrations from 25 to 150 mg/L was from 10 to 30 min, respectively, but all experiments in this study were carried after 30 min. The biosorption process was relatively faster; this shows their good kinetic properties. On the other hand, the amount of cadmium ions biosorbed decreases with the increase of KCL salt and particle size. The experimental data for the biosorption kinetics were found to conform to pseudo-second-order kinetics model with a good correlation.

The negative values of ΔG° at different temperatures show that the biosorption process is a spontaneous process. An enthalpy change is positive which further confirms that the process is endothermic nature of the biosorption-interaction. Consequently, the results of this study will be useful for using this waste material as an economic and a nonhazardous bio-material for the removal of heavy metals as cadmium and mercury in wastewater treatment.

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References

- [1] S.E. Bailey, T.J. Olin, R.M. Bricka, D. Dean Adrian, A review of potentially low- cost sorbents for heavy metals, *Water Res.*, 33 (1999) 2469–2479.
- [2] L. Nouri, O. Hamdaoui, Ultrasonication-assisted sorption of cadmium from aqueous phase by wheat bran, *J. Phys. Chem.*, 111 (2007) 8456–8463.
- [3] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse an agricultural waste, *Water Res.*, 36 (2002) 2304–2318.

- [4] E.-K. Guechi, D. Beggas, Removal of cadmium(II) from water using fibre fruit lufa as biosorbent, *Desal. Water Treat.*, 94 (2017) 181–188.
- [5] D. Mohan, C.U. Pittman Jr., M. Bricka, F. Smith, B. Yancey, J. Mohammad, P.H. Steele, M.F. Alexandre-Franco, V. Gómez-Serrano, H. Gong, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, *J. Colloid Interface Sci.*, 310 (2007) 57–73.
- [6] E.-K. Guechi, S. Benabdesselam, Removal of cadmium and copper from aqueous media by biosorption on cattail (*Thypha angustifolia*) leaves: kinetic and isotherm studies, *Desal. Water Treat.*, 173 (2020) 367–382.
- [7] I.S. Bădescu, D. Bulgariu, I. Ahmad, L. Bulgariu, Valorisation possibilities of exhausted biosorbents loaded with metal ions—a review, *J. Environ. Manage.*, 224 (2018) 288–297.
- [8] L. (Negrilă) Nemeş, L. Bulgariu, Optimization of process parameters for heavy metals biosorption onto mustard waste biomass, *Open Chem.*, 14 (2016) 175–187.
- [9] S. Rangabhashiyam, E. Nakkeeran, N. Anu, N. Selvaraju, Biosorption potentials of a novel *Ficus auriculata* leaves powder for the sequestration of hexavalent chromium from aqueous solutions, *Res. Chem. Intermed.*, 41 (2015) 8405–8424.
- [10] D. Mohan, C.U. Pittman Jr., P.H. Steele, Single, binary and multicomponent adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent, *J. Colloid Interface Sci.*, 297 (2006) 489–504.
- [11] L. Semerjian, Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust, *J. Hazard. Mater.*, 173 (2010) 236–242.
- [12] B.S. Inbaraj, N. Sulochana, Carbonised jackfruit peel as an adsorbent for the removal of Cd(II) from aqueous solution, *Biores. Technol.*, 94 (2004) 49–52.
- [13] S. Asma, I. Muhammad, H.H. Wolfgang, Kinetics, equilibrium and mechanism of Cd²⁺ removal from aqueous solution by mungbean husk, *J. Hazard. Mater.*, 168 (2009) 1467–1475.
- [14] M. Aqeel Ashrafa, M. Abdur Rehman, Y. Alias, I Yusoff, Removal of Cd(II) onto *Raphanus sativus* peels biomass: equilibrium, kinetics, and thermodynamics, *Desal. Water Treat.*, 51 (2013) 4402–4412.
- [15] M.M. Figueira, B. Volesky, V.S.T. Ciminelli, F.A. Roddick, Biosorption of metals in brown seaweed biomass, *Water Res.*, 34 (2000) 196–204.
- [16] C. Duan, N. Zhao, X. Yu, X. Zhang, J. Xu, Chemically modified kapok fiber for fast adsorption of Pb²⁺, Cd²⁺, Cu²⁺ from aqueous solution, *Cellulose*, 20 (2013) 849–860.
- [17] G. Akkaya, F. Guzel, Bioremoval and recovery of Cu(II) and Pb(II) from aqueous solution by a novel biosorbent water melon (*Citrullus lanatus*) seed hulls: kinetic study, equilibrium isotherm, SEM and FTIR analysis, *Desal. Water Treat.*, 51 (2013) 7311–7322.
- [18] E.-K. Guechi, F. Bendebane, A. Aisset, R. Malaoui, Sorption of mercury(II) from aqueous solution by Okoume sawdust, *Desal. Water Treat.*, 38 (2012) 285–292.
- [19] E.-K. Guechi, Equilibrium, kinetics and mechanism for the removal of Rhodamine B by adsorption on Okoume (*Aucoumea Klaineana*) sawdust from aqueous media, *Desal. Water Treat.*, 94 (2017) 164–173.
- [20] E.-K. Guechi, O. Hamdaoui, Biosorption of methylene blue from aqueous solution by potato (*Solanum tuberosum*) peel: equilibrium modelling, kinetic, and thermodynamic studies, *Desal. Water Treat.*, 57 (2016) 10270–10285.
- [21] B.H. Hameed, M.I. El-Khaiary, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: equilibrium isotherms and kinetic studies, *J. Hazard. Mater.*, 154 (2008) 237–244.
- [22] T.S. Anirudhan, P. Senan, M.R. Unnithan, Sorptive potential of a cationic exchange resin of carboxyl banana stem for mercury(II) from aqueous solutions, *Sep. Purif. Technol.*, 52 (2007) 512–519.
- [23] H. Demir, A. Top, D. Balkose, S. Ulku, Dye adsorption behavior of Luffa cylindrical fibers, *J. Hazard. Mater.*, 153 (2008) 389–394.
- [24] V.J.P. Poots, G. McKay, J.J. Hzaly, The removal of acid dye from effluent using natural adsorbant—I PEAT, *Water Res.*, 10 (1976) 1061–1066.
- [25] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, *J. Hazard. Mater.*, 142 (2007) 144–152.
- [26] I. Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark, *J. Hazard. Mater.*, 152 (2008) 148–158.
- [27] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, *Chem. Eng. J.*, 151 (2009) 255–261.
- [28] E. Nakkeeran, N. Saranya, M.S. Giri Nandagopal, A. Santhiagu, N. Selvaraju, Hexavalent chromium removal from aqueous solutions by a novel powder, prepared from *Colocasia esculenta* leaves; *Int. J. Phytorem.*, 18 (2016) 812–821.
- [29] G. Owes El-Sayed, Removal of methylene blue and crystal violet from aqueous solutions by palm kernel-fiber, *Desalination*, 272 (2011) 225–232.