Cadmium(II) ions removal using dried banana bunch powder: experimental, kinetics, and equilibria

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ABSTRACT

The heavy metals removal is an important issue in environmental cleaning from pollutants, and the use of cheap and ecofriendly materials was a millstone in wastewater treatments. Banana bunch dried powder (BBDP) characterized by Fourier transform infrared, X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis (EDAX), and particles size analyses, which showed that it characterized by the presence of different compounds such as lignin, cellulose and hemicelluloses. The BBDP particles size falls in a wide range started from less than 40 nm up to 1 μm. However, the mean particles size is located around 220 nm where the beak is recognized. The capability of the use of banana bunches was collected from the market for removing Cd(II) was examined. BBDP can be easily applied as a cheap biosorbent for Cd(II). The BBDP adsorbed the Cd(II) in high efficiency by varying the parameters. The adsorption of cadmium ions was verified using elemental analysis (EDAX) of the BBDP sorbent before and after the adsorption process. Maximum removal of Cd(II) was reached after 3 h at optimum pH 4, and 150 rpm was found 98%. The kinetic and equilibrium results for Cd(II) ions sorption with different concentrations using BBDP were analyzed. The sorption results indicated that it was a process of second order with ion-exchange mechanism. The maximum sorption capacity at 25°C was found as 87 mg/g, according to the Langmuir isotherm. Moreover, the diffusion rate was elaborated using intraparticle models and particulate of Dumwald–Wagner. Boyd kinetic expression analyzed the sorption data for determining the actual step of rate-controlling.

Keywords: Cadmium; Wastewater; Banana bunch; Batch sorption; Kinetic model; Isothermal model

1. Introduction

Environmental pollution is a very dangerous and increasing problem in developing countries, where there are no technologies for wastewater treatment. The environmental pollution with heavy metals is persuasion worldwide with advances in the industry. Many heavy metals like nickel, copper, cadmium, and chromium are known as the commonest toxic heavy metals, which used and the prevalence of environmental contaminants [1,2]. Low concentrations of those metals are essential as enzymes' co-factors, while high concentrations cause high toxicity to the living cells through inhibition of metabolism.

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The techniques used for heavy metals removing such as lime coagulation, reverse osmosis, chemical precipitation, ion exchange, and solvent extraction are often ineffective, high cost, and highly harmful to the environment with comparing to adsorption. Nowadays agricultural wastes are receiving great attention as adsorbents for toxic metals from industrial wastewater in general and Cd(II) especially [3–6]. Biosorption is an alternative to the used environmental technologies in removing and recovery of heavy toxic ions from solutions [7].

Metal accumulation generally falls into two categories, biosorption up-taking by not growing, nonliving biomasses and biomasses products, and living organisms' bioaccumulation [1,8–10]. The heavy metals come as a result of a wide range of industries. The type and amount of the heavy metal's wastes depend on the industrial sources.

Drainage of toxic metals from many industries has impacts stresses on the environment. Ordinary treatments for removing toxic metal from solutions are non-economic and produce a large amount of harmful sludge. Biosorption using non-living microbial or plant origin biomass is a new and alternate method in removing these toxic metals from solutions [11].

The removal of several varieties of contaminants from the environment needs attention to understand the importance of different paths and regulations of carbon in the environment and for certain materials and they will enhance the development of bioremediation methods and transformation pathways [12].

To design sorption columns for industrial-scale application, the kinetics of the batch sorption must be explored. The system operational conditions in addition to the chemical and physical characters of the adsorbent system are determined factors controlling the nature of the sorption process. Among many kinetic models, Elovich, diffusion model, and first- and second-pseudo-orders have been used mostly in studying the sorption process mechanism [13–15].

To understand the adsorption process, information of essential adsorption equilibria is needed to help in providing the basic physicochemical data to evaluate the adsorption process applicability. Two common isotherm models usually used namely Freundlich and Langmuir isotherms [16].

This study aims to develop cheap and eco-friendly BBDP sorbent for Cd(II) removal from wastewaters. The study focused on the characterization of the BBDP sorbent composition using Fourier transform infrared (FTIR), energy dispersive X-ray analysis (EDAX), and scanning electron microscopy (SEM) and studying the factors that enhance the adsorption process. Furthermore, the data of the Cd(II) adsorption process have been analyzed using kinetic and isotherm models for best understanding of the sorption process characters and evaluation of its applicability.

2. Materials and methods

2.1. Preparation of cadmium solution

To prepare the stock solution, 100 mg of $Cd(NO_3)_2$ was dissolved in 50 mL of 10% HNO₃, then complete to 1 L with distilled water in a volumetric flask (50 µg Cd/mL). For the working solution, 10 mL of the stock solution was completed to 1 L with 1% HNO_3 (1 µg Cd/mL).

2.2. Banana bunch dry powder preparation

The banana bunches were collected from the local markets, then were cut into small pieces, washed with distilled water and dried at 80°C for 2 d. The chemical activation was done using H_2SO_4 at moderate temperature to produces a large surface area and a high degree of porosity according to the method described by Santhi et al. [17]. The dried bunches were crushed, sieved (200 nm) and then stored in a desiccator until use.

2.3. Characteristics of BBDP adsorbing material

The adsorbent will be characterized by:

2.3.1. Fourier-transform infrared spectroscopy

It was used to investigate the chemical structure of BBDP. The BBDP was prepared as KBr pellets and the spectra were measured using frequency range (400–4,000 cm⁻¹) and the IR spectra were recorded on a Smart iTR.

2.3.2. X-ray diffraction

The dried particles of BBDP were analyzed using XRD. The patterns were measured at the range of 10–90 and at 5 min⁻¹ speed.

2.3.3. Scanning electron microscopy

The BBDP particles were examined by coating with a thin gold layer under reduced pressure. The morphology of surface was visualized at 1,500× magnification using JEOL/JSM-6335F SEM.

2.3.4. Energy dispersive X-ray analysis

To verify the adsorption of cadmium ions, the composition (mass ratios) of the developed sorbent before and after the adsorption process was examined by EDAX using analytical SEM (Joel Jsm 6360LA, Japan).

2.3.5. Particle size analysis

0.1 g of the developed BBDP sorbent was dispersed in 10 mL distilled water. Each sample was sonicated using ultrasonic water bath for 15 min before measured in submicron particle size analyzer (Beckman Coulter N5, USA).

2.4. Sorption experiments

The experiments were carried out using 50 mL of the synthetic Cadmium aqueous solution and 0.5 g of DBBP in 250 mL bottles. The bottles were shaken for 3 h at room temperature and 150 rpm. Filtration was carried out to separate the adsorbents and solutions using Whatman no. 42 filter paper. The resulting filtrate was stored at 4°C till use. The residual cadmium ion was also determined using atomic absorption spectrophotometry (AAS) method.

2.4.1. Cadmium concentration

Different concentrations of Cd(II) ions (50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mg/L) were used to evaluate

the optimum concentration to be removed by the adsorbent. The BBDP as adsorbent was incubated with the different concentrations of Cd(II) ions for 30 min at room temperature.

2.4.2. Adsorbent amount

Different amounts of BBDP as adsorbent (0.5, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.0 g) were used to evaluate the optimum amount. The optimum Cd(II) ions concentration was incubated with the different BBDP amounts for 30 min at room temperature.

2.4.3. Time course

The adsorption experiment was carried out at time intervals (min): 30, 60, 90, 120, 150, and 180 to evaluate the proper time at which maximum adsorption was occurred. The optimum Cd(II) ions concentration and BBDP amount were used and the experiment was incubated at room temperature.

2.4.4. Agitation speed

Different agitation speeds were used (rpm): 150, 200, 250, 300, 350, and 400 to determine the optimum agitation speed at which maximum biosorption. The optimum time, Cd(II) ions concentration and BBDP amount were used and the experiment was incubated at room temperature.

2.5. Sorption kinetic models

The kinetics of biosorption process were described using three linear kinetic models. The pseudo-first-order kinetic model [18]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{1}$$

The pseudo-second-order rate (chemisorptions) [19]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \tag{2}$$

The simple Elovich model [20]:

$$q_t = \alpha + \beta \ln t \tag{3}$$

where q_e and q_t are the adsorbed ions quantity (mg/g) and t time (min) at equilibrium. k_1 (min^{-1}) is the constant of first-order reaction rate. α is the rate of initial sorption (mg/g min) and β is the surface coverage extent and activation energy of chemisorption (g/mg). k_2 is the equilibrium constant rate of second-order reaction (g/mg min).

2.6. Sorption mechanisms

The sorption mechanism has been followed using three models. The Dumwald–Wagner model, where F is the adsorption percent (q_t/q_e) and K is the diffusion rate constant [21]:

$$\log\left(1 - F^2\right) = -\left(\frac{K}{2.303}\right) \times t \tag{4}$$

The intraparticle model where k_d is the intraparticle diffusion rate and C is the boundary layer indicator thickness [22]:

$$q_t = k_d t^{1/2} + C \tag{5}$$

The actual step of rate-controlling in the sorption process is detected by Boyd et al. model [23]:

$$F = 1 - \left(\frac{6}{\pi^2}\right) \exp\left(-B_t\right) \tag{6}$$

We can calculate F (the solute adsorbed fraction at different time t) and its mathematical function B_t using the following equations:

$$F = \frac{q}{q_\alpha} \tag{7}$$

$$B_t = -0.4978 - \ln\left(1 - \frac{q}{q_\alpha}\right) \tag{8}$$

where q and q_α are the adsorbed amount (mg/g) at equilibrium and time t.

2.7. Sorption isotherm models

The most commonly isotherm models used in almost all the publications deal with characterization of adsorption process are Freundlich [24] and Langmuir isotherm models [25]. The two models are opposite to each other.

The Freundlich isotherm model is the first used isotherm model which postulates site energies of heterogeneous surfaces and multi-layers levels of sorption. The mathematical linear formula of the model is expressed as the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n_f} \ln C_e \tag{9}$$

where q_e (mg/g) and C_e (mg/L) represented the adsorbent capacity and the adsorbate ions concentration at equilibrium. The indicators of the adsorption capacity and adsorption intensity are given by K_F and n_f Freundlich constants.

Furthermore, the Langmuir isotherm assumes that surface is completely homogeneous with a limited similar sites number with negligible interaction impact between adsorbed molecules which results in sorption of monolayer. The linear mathematical formula of the model is presented by the equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{10}$$

where q_m is the maximum adsorption capacity (mg/g) of monolayer and K is the energy of sorption (L/mg). To predict the favorable or unfavorable of the adsorption system, essential characteristics defined by a dimensionless separation factor (R_L) used and calculated using the following equation [26]:

$$R_L = \frac{1}{1} + KC_0 \tag{11}$$

where C_0 is the initial Cd(II) ions concentration (mg/L).

There are another isotherm model in between the Freundlich and Langmuir isotherm models such as the D–R isotherm and the Temkin isotherm. The D–R isotherm is derived from the Langmuir isotherm, it is more general where rejects the constant adsorption potential assumption [27]. The isotherm model of D–R is expressed as follows:

$$\ln q_e = \ln V'_m - K'\varepsilon^2 \tag{12}$$

The equilibrium adsorption capacity is q_e (mg/g), the sorption capacity of D–R is V'_m (mg/g), the adsorption energy constant is K' (mol²/kJ²), and ε is the Polanyi potential. ε is calculated using the following equation:

$$\varepsilon = RT\left(1 + \frac{1}{C_e}\right) \tag{13}$$

The gas constant ($R = 8.314 \times 10^{-3}$ kJ/mol K) and the temperature T(K). Information about the nature of the sorption process can obtained from the model through calculating the energy needed to transfer one molecule of the sorbate from the solution phase to the surface of the solid phase (E) [28] according to the following equation [29]:

$$E = (2K')^{-0.5} \tag{14}$$

The Temkin isotherm model considers the indirect sorbent/sorbate interactions impact on the sorption process which reduced in a linear way the sorption heat of all molecules in a layer [30]. The linear form expressed as follows [31]:

$$q_e = B\ln K_T + B\ln C_e \tag{15}$$

where B is the sorption heat constant and K_T represents the maximum binding energy.

3. Results and discussion

Cadmium (Cd) is considered as lethal heavy metal of environmental worry and work-related which recognized as a carcinogenic and teratogenic substance to human. According WHO [32] the permissible limit is 3.0 ppb for Cd in drinking water.

3.1. Characteristics of BBDP adsorbing material

3.1.1. FT-IR spectrum

The characteristic band appeared in IR of BBDP was broad and strong band for hydroxyl groups and residual moisture (v O–H) at 3,339 cm⁻¹ which is typical to carbohydrates, and due to vibration of methylene groups (v C–H), a small band at 2,919 cm⁻¹ was detected, both groups enable this substance to be chelating agents for heavy metals (Fig. 1). The broad absorption corresponding to the stretching of H-bonded OH groups at 3,300 cm⁻¹ and C–H groups at 2,900 cm⁻¹ [33–35]. There was a small band of C–C skeletal vibration at 1,612.75 cm⁻¹, peak of carbonyl stretching (C=O) corresponded to acetyl groups as in hemicelluloses and for the aldehyde group as in lignin at 1,630 cm⁻¹ [36,37].
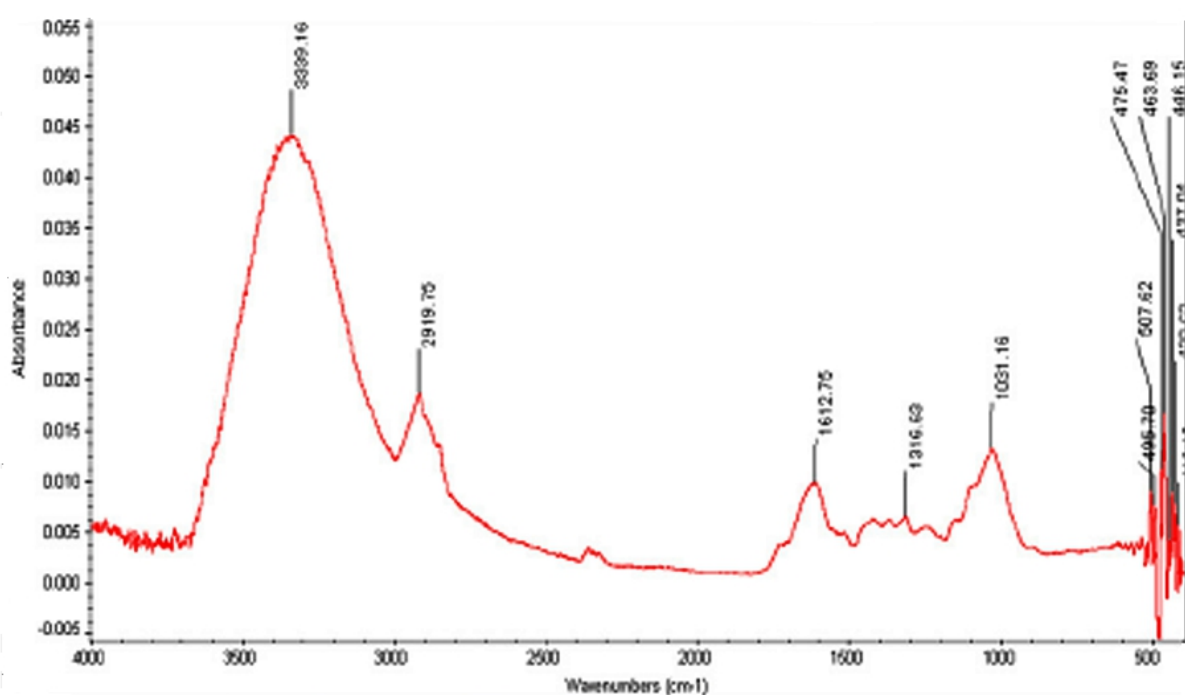

Fig. 1. FT-IR spectrum of the sorbent BBDP particles.

C(O)–O stretching at 1,316.63 cm^{-1} and C–H bending at 1,375 cm^{-1} [38]. Typical glucose residue of disaccharide and C–O stretching at C–6 was observed at 1,031.16 cm^{-1}. The bands at 1,031.70; 1,254.34; and 1,422.51 cm^{-1} are characteristics for the COOH and OH groups stretching vibrations [36,39,40]. The peak of C–O stretching at C–6 was detected at 1,031 cm^{-1}. C–O covalent bonds, O–H linkages, and C–O–C stretching were shown at the peaks between 1,000 and 1,200 cm^{-1} which indicated to hemicellulose, cellulose, and lignin [41].

3.1.2. XRD analysis

The spectra of XRD showed the presence of carbon, α-quartz, β-quartz, and cristobalite due to the presence of distinguished peaks at 16° 2θ and 21.4° 2θ, confirmed the presence of and high carbon concentration and peaks at 2θ = 28.9° and 35° indicating the partial crystallization from the amorphous state commenced, also a small peak at 35° 2θ (Fig. 2). Kwon et al. [42] found that peak at 21.6° 2θ
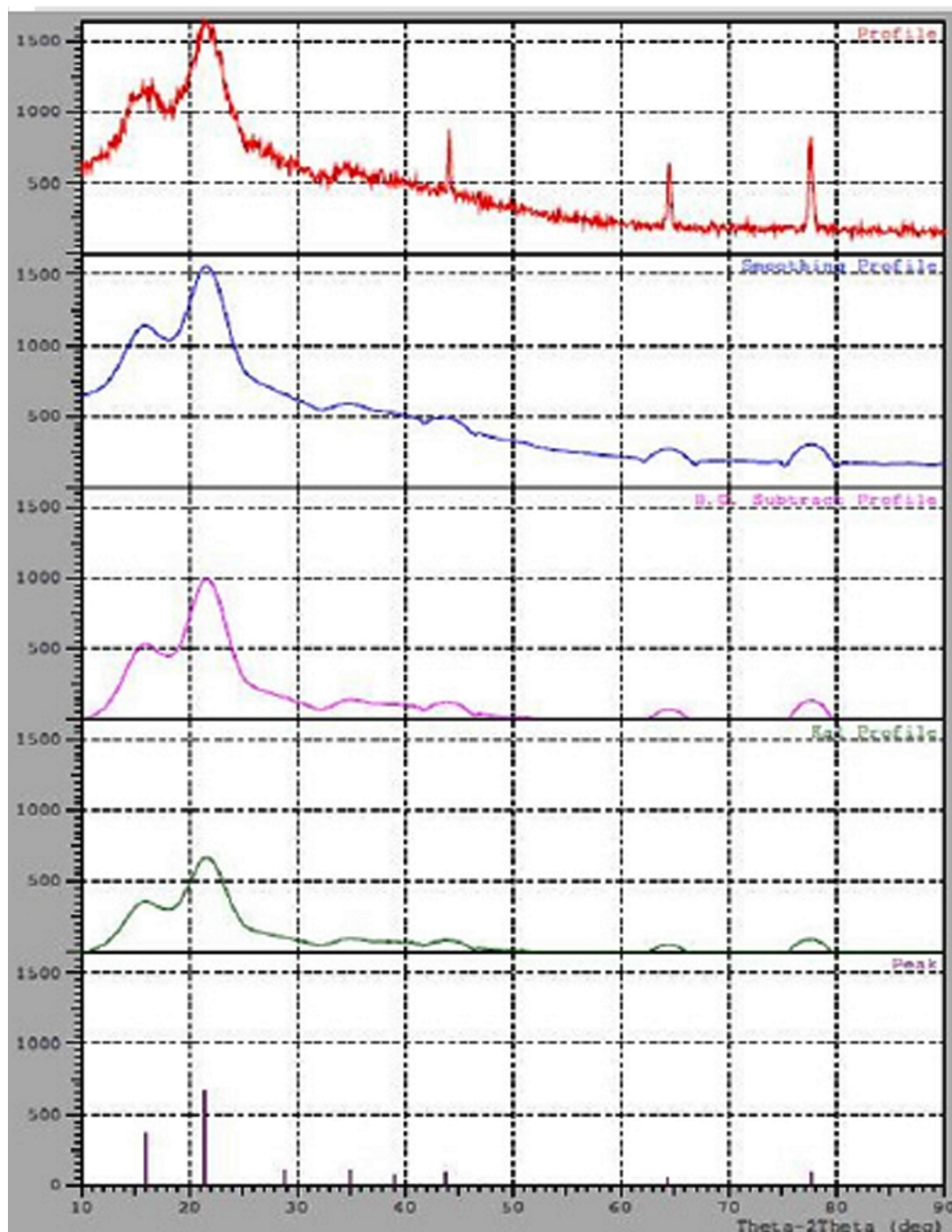

Fig. 2. XRD analysis of sorbent BBDP particles.

and peaks between 22° and 28° 2θ, which confirms highly carbon concentration, the amorphous phase contains sulphur and quartz, respectively. A small peak of cristobalite at 31.4° 2θ was observed. The peak at 27.4° 2θ in both acid-treated fly ash (AFA) and polyelectrolyte-coated fly ash (PEFA), respectively, indicating the presence of β-quartz.

3.1.3. SEM microphotograph analysis

The thermal decomposition lead to the release of lignin, hemicellulose, and organic matter, with cracking and shrinkage leading to the porosity improve of the materials [43,44]. The SEM image of the BBDP sample showed highly heterogeneous surface with structurally complex network of pores and channels, with a parallel fibrous of different diameters ranged from 3 to 6 μm. The fibrous surface loaded with white heterogeneous particles of silicates with varied size up to 1 μm. The pores size ranged from 10–20 μm (Fig. 3). These observations are in accordance with that observed by Dehkhoda et al. [45] in biochar. It is worthy to mention here that the porosity and surface area properties are the key function in sorption process including the heavy metals.

3.1.4. Particle size analysis

The analysis of the developed BBDP sorbent particle size in Fig. 4 show that the particles size falls in a wide range started from less than 40 nm up to 1 μm. However, the mean particles size is located around 220 nm where the peak is recognized. Particles with size ≥200 nm were used to guarantee moderate surface area for the adsorption process.

3.1.5. Energy dispersive X-ray analysis

The elemental analysis of the developed BBDP sorbent before and after the adsorption process is presented in Figs. 5a and 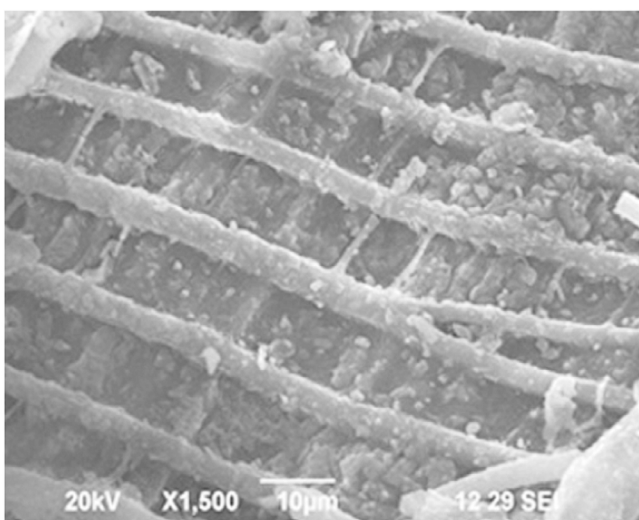b show mainly the presence of C, N, Si, S, and Cd elements. Since the adsorption process of cadmium ions will be mainly added of the adsorbed Cd ions to the structure of the BBDP sorbent after completion of the adsorption process, C and Cd weight ratio has been presented in Table 1. From it is clear, that the Cd weight (%) after adsorption has been increased with decrease of the C weight ratio. These results confirmed the success of the Cd ions adsorption process.

3.2. Sorption experiments

3.2.1. Effect of Cd(II) concentration

The removal percentage of Cd(II) ions by BBDP as adsorbent was increased by increasing the concentration of Cd(II) ions. From the results, the removal of Cd(II) ions had the highest percent of removal (97.9%) at the end of 30 min in 350 mg/L (Fig. 6a). The copper removal efficiency decreased by increasing the initial copper concentration, while the lowest efficiency was attained at the maximum copper concentration of 500 mg L^{-1}. This may have been due to the high amount of metal ions that exceeded the available binding sites in *Mesorhizobium amorphae* [46]. This means that a competition increased between metal ions on the available binding site [47].

3.2.2. Effect of BBDP amount

The BBDP concentration of 1.75 g gave the highest Cd(II) ions removal percentage (98.4%) (Fig. 6b). When the surface area of BBDP increased, the Cd(II) ions amount adsorbed increased and vice versa [48–51]. This claim should be supported by concrete data to the surface area value of BBDP. This is due to the increase in the binding sites available in the biomass biosorbent for the heavy metal's complexation [52]. This would explain the high percentage removal of Cd(II) ions. In most cases, lower biosorbent dosage yielded higher uptake and lower efficiency of removal [53].

Table 1
Elemental analysis of C and Cd for the BBDP developed sorbent before and after the adsorption process

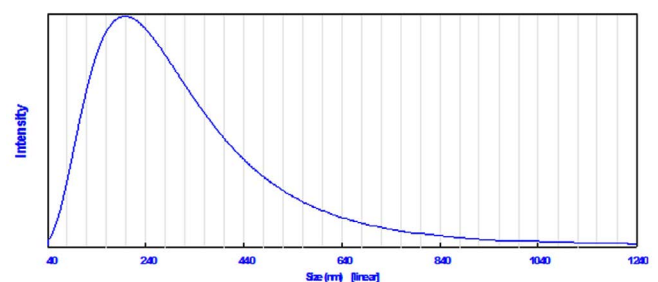| BBDP sorbent	C (wt.%)	Cd (wt.%)
Before	99.54	00.46
After	99.30	00.70

Fig. 3. SEM image of sorbent BBDP particles.

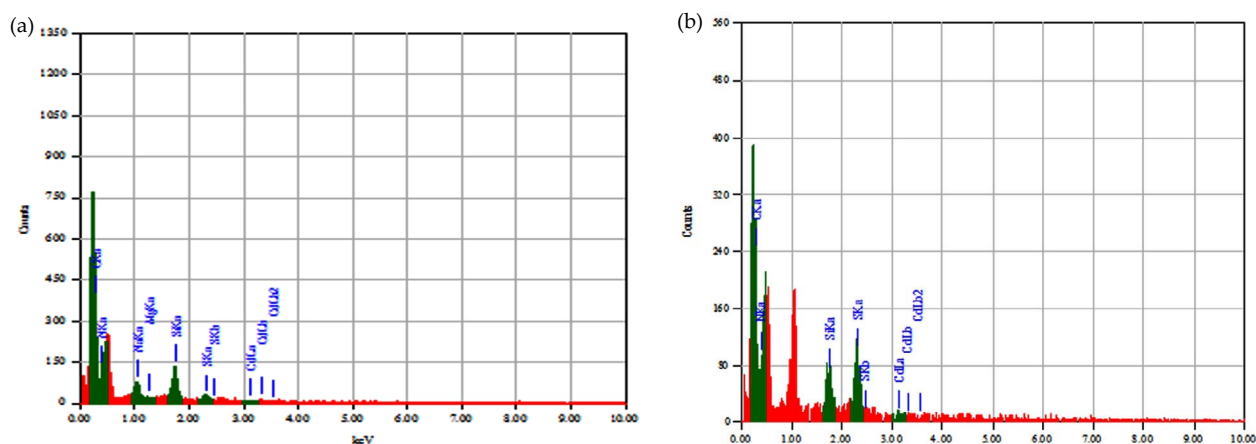Fig. 4. BBDP sorbent particle size distribution.

Fig. 5. Elemental analysis of BBDP sorbent (a) before and (b) after cadmium adsorption.
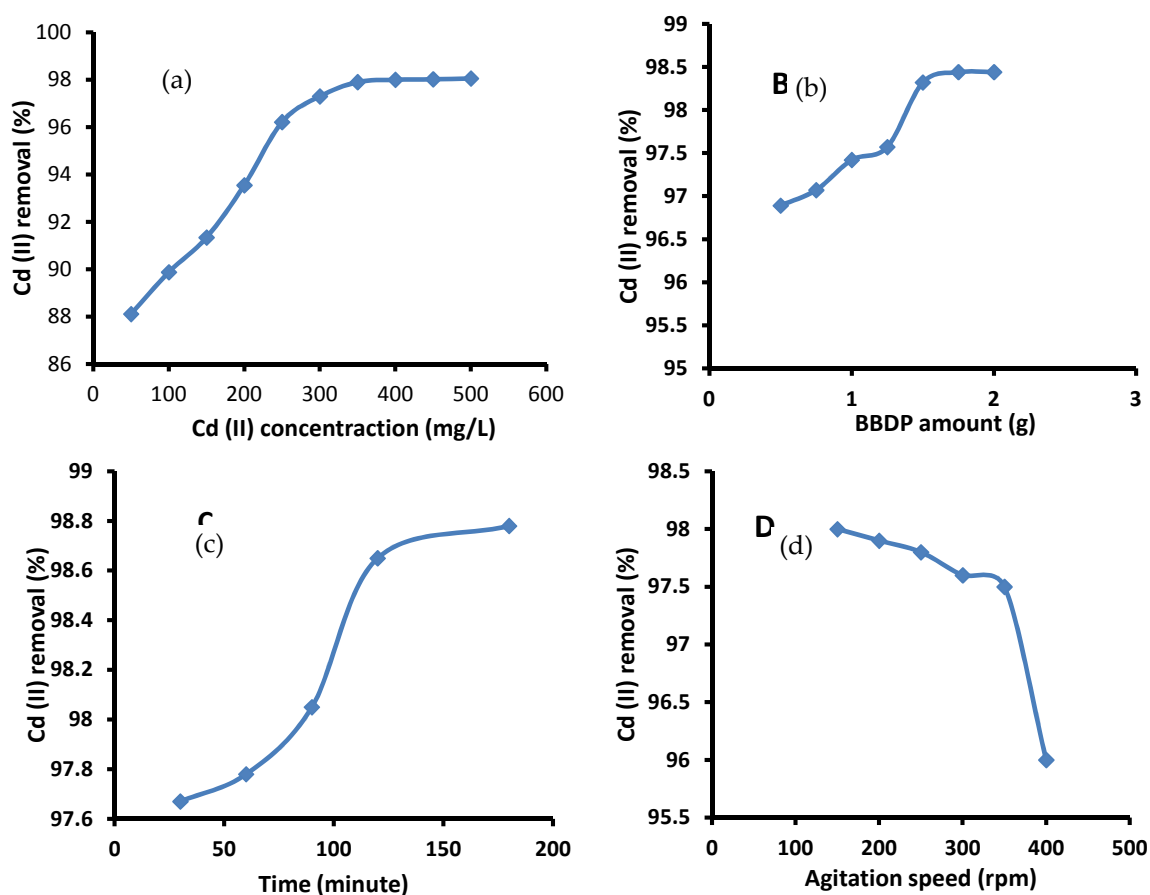

Fig. 6. Optimization of the factors affecting the removal of Cd(II) using BBDP. (a) Cd(II) ions concentrations, (b) BBDP amounts, (c) time, (d) agitation speed.

3.2.3. Effect of contact time

By using the optimum Cd(II) ion and BBDP concentrations, there was a progress in the removal percent of Cd(II) ions with time in the solution. From Fig. 6c, Cd(II) ions had the highest percentage of removal (98.78%) at the end of 180 min in 350 mg/L concentration. As equilibrium time is the most important parameter economically,

so this result is significant for wastewater treatment system. The biosorption was fast for the first hour due to the binding sites availability on the biomass, while the time of equilibrium extended to 48 h [54]. The metal ions biosorption described as a biphasic process [55], the rapid phase takes place due to adsorption on the surface of the biomass, while the slow one due to the metal ion diffusion into the biomass inner part [55].

3.2.4. Effect of agitation speed

The results in Fig. 6d showed that the sorption rate of BBDP decreased with agitation increase, the obtained results from the sorption experiment showed that the highest rate of sorption by BBDP for Cd(II) was achieved in the solution at 150 rpm. With increase in rpm, the protonation degree of the sorbent functional group gradually decreased and consequently the removal of Cd(II) ions was decreased. There are relationship between the sorbents surface basis and the anions. If the speed increases, the sorption decreases. In some cases, external film diffusion can influence the rate of biosorption process. Constant agitation can minimize this mass transfer resistance. It was found that biosorption of copper by CCNWGS0123 was more effective with moderate agitation [56,57].

3.3. Sorption kinetic models

The model of pseudo-first-order kinetic is presented in Fig. 7a. The first order-rate constant k_1 is 0.0234. The calculated q_e value from the equation (19.6 mg/g), which is different from the experimental value (592.7 mg/g), confirms that this model is not fit to this sorption process where the correlation coefficient is not high (0.7263).

The chemisorption kinetics is given in Fig. 7b. From the Fig. 7, the value of k_2 is 0.0012. Additionally, the very close values of $q_{e,calculated}$ (588.23 mg/g) with that obtained from the experimental data (592.7 mg/g) indicating that the Cd(II) sorption kinetics onto BBDP was well-described by second-order equation where the value of the correlation coefficients, R^2 (1) was extracted, which suggests the limiting step rate in these sorption processes may be chemisorption's through the sharing or exchanging of electrons between sorbent and sorbate [58].

Fig. 7c illustrates the simple Elovich model. The value of β (4.0806 g/mg) indicated the number of sites available for sorption while α is the sorption quantity (571.13 mg/g) when ln$t$ is equal to zero, that is, the sorption quantity when t is 1 h. This value clarifies the sorption behavior of the first step [59]. Also, it was declared that the Elovich equation fits well with the experimental data regardless the low correlation coefficients value (R^2) 0.8302.

3.4. Sorption mechanisms

The limitation of the above-mentioned models in describing the diffusion mechanism makes us investigate different adsorption models. Since mass action is a very
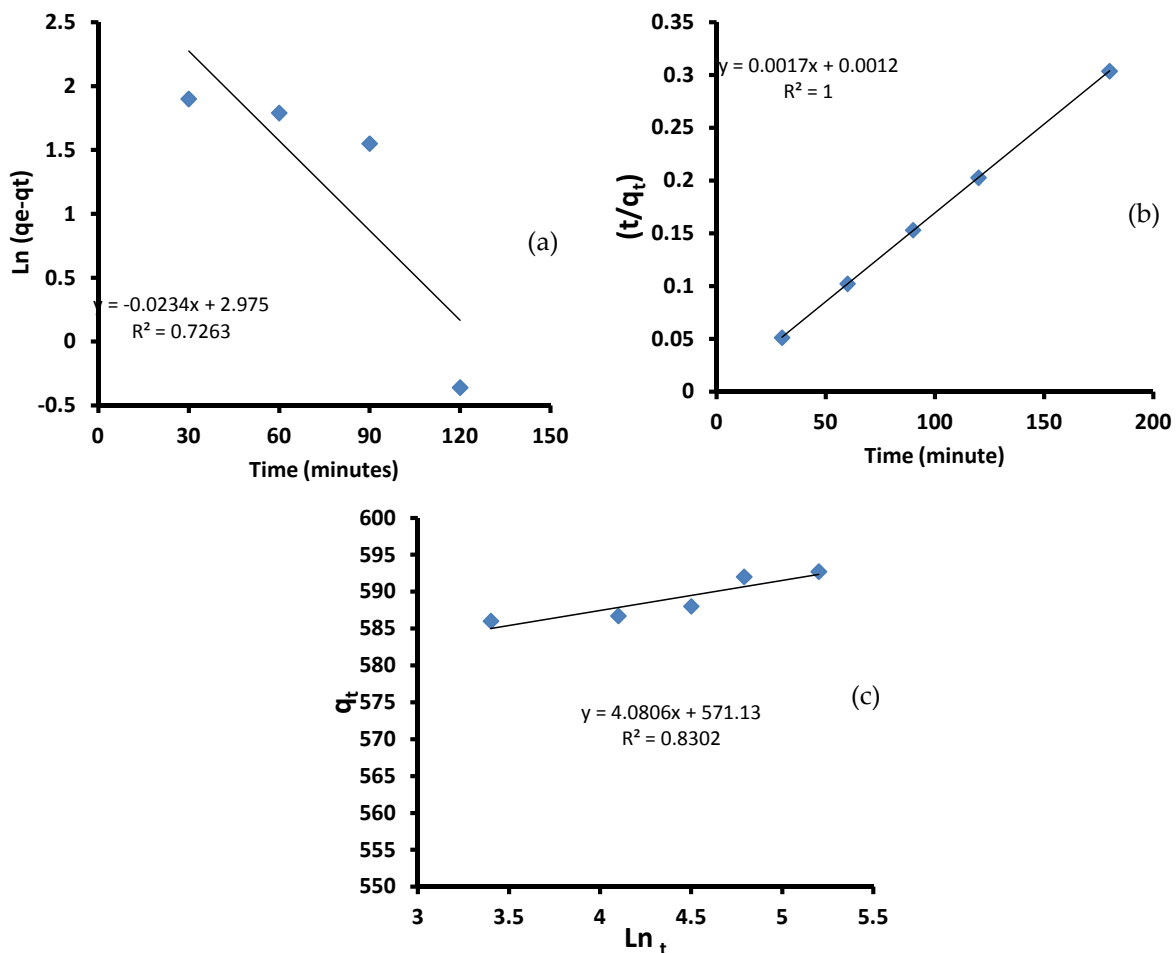

Fig. 7. Sorption kinetic models for Cd(II) ions removal using BBDP. (a) first order, (b) second order, (c) simple Elovich.

fast process, so only the film and intraparticle diffusion are left to describe the liquid/solid sorption process, that is, one of these processes must be the rate limiting step [60]. The equation of diffusion rate intra-particle and inside particles of Dumwald–Wagner models were used to calculate the rate of diffusion, and the Boyd model was examined to determine the actual rate-controlling step for the Cd(II) ions sorption.

The Dumwald–Wagner kinetic model is presented in Fig. 8a. The constant of diffusion rate for Cd(II) ions diffused inside BBDP were $R^2 = 0.7263$ and $K = 2.74$.

The intraparticle diffusion model indicated two separate linear portions (Fig. 8b). This suggested that the process of sorption consists of surface adsorption and intraparticle diffusion together, while the first linear portion indicates the effect of boundary layer and the second linear portion is the result of intraparticle diffusion [23]. The intraparticle diffusion rate k_d (0.2846) was calculated from the slope of the second linear portion. The value of C (588.88 mg/g) gives an information about the boundary layer thickness. The larger the intercept, the greater the effect of boundary layer [61].

Finally, the actual rate-controlling step was determined by Boyd et al. [24] as presented in Fig. 8c. The straight line obtained, which does not pass through the origin, indicating that film diffusion governs the limiting process rate [62].

3.5. Sorption isotherm models

The Freundlich isotherm is a vastly equilibrium isotherm model used, on the contrary to the Langmuir model, it does not give any information on the sorption capacity of monolayer [25,63,64]. Fig. 9a gives the constants values of n_f and K_F, as 0.68 and 1.45. The n_f value was found that $n_f < 1$ indicated less appropriate sorption for Cd(II) ions using the BBDP [65].

The Langmuir model is presented in Fig. 9b where the R^2 value is 0.9234 where indicates a good mathematical fit. The calculated value of q_m is 86.96 (mg/g) indicates that the BBDP was highly efficient for Cd(II) ions removal and the K value is 5.83 (L/mg) indicates the moderately low sorption energy (5.83 L/mg). The calculated values of R_L and the main characteristics of the Langmuir isotherm, show appropriate sorption because the values of R_L are between 0 and 1 [66] and confirming the preferable of the Langmuir model used under the study conditions (Table 2).

The D–R isotherm, the D–R plot produced a straight line with the R^2 value equal to 0.8555, which indicated that the D–R model does not fit the experimental data compared with the Langmuir and Freundlich isotherm model. As claimed by the plot of D–R isotherm model, the parameters V'_m, K', and E are equal to 105.7 mg/g, 0.013 mol^2/kJ^2,
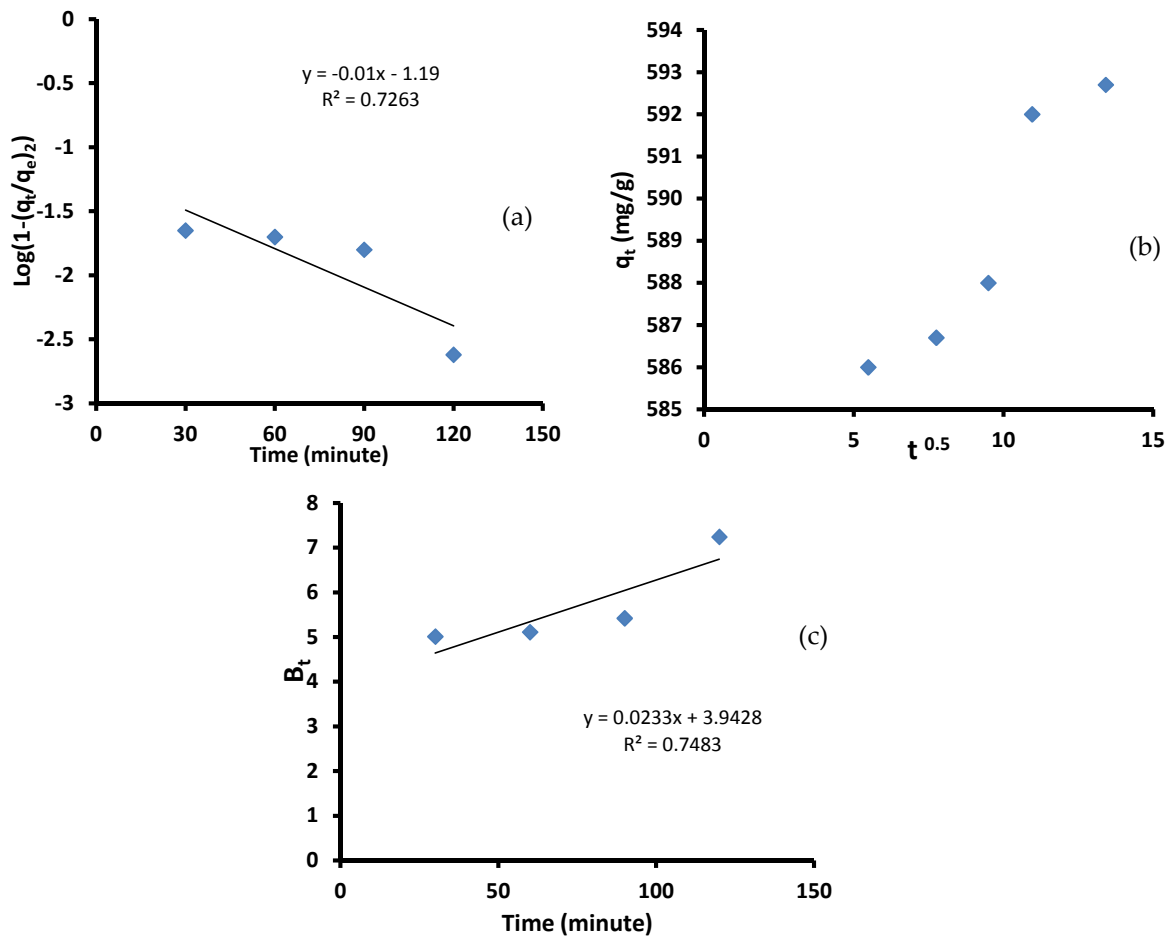

Fig. 8. Sorption mechanisms for Cd(II) ions diffusion in BBDP using different models. (a) Dumwald-Wagner model, (b) intraparticle diffusion, (c) Boyd expression.

and 0.161 kJ/mol, respectively (Fig. 9c). The calculated sorption energy ($E < 8$ kJ/mol) indicated that the Cd(II) ions sorption process might be physisorption in nature [67]. Thus, it is likely that the physical means such as electrostatic forces played an important role in sorption mechanisms for the Cd(II) ions sorption in this work.

The Temkin isotherm is illustrated in Fig. 9d. The calculated value of K_T is 0.049 L/g, and the constant B, which is 350.34 J/mol, is associated to the sorption heat.

Finally, the fitness of the isotherm models is summarized in Table 3 according to the R^2 values. The Langmuir model produced the highest value of R^2 (0.9234) and this described that Cd(II) ions sorption on the BBDP was best by this model, which monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules.

3.5. Adsorption capacity comparative study

Table 4 shows a comparative study of the Cd(II) removal using different origin activated carbon adsorbents

Table 2
R_L values for different initial cadmium ions concentrations

Cd(II) (ppm)	R_L
150	0.001142
200	0.000857
250	0.000686
300	0.000571
350	0.00049
400	0.00003

Table 3
R^2 values for cadmium removal with the different studied equilibrium isotherms

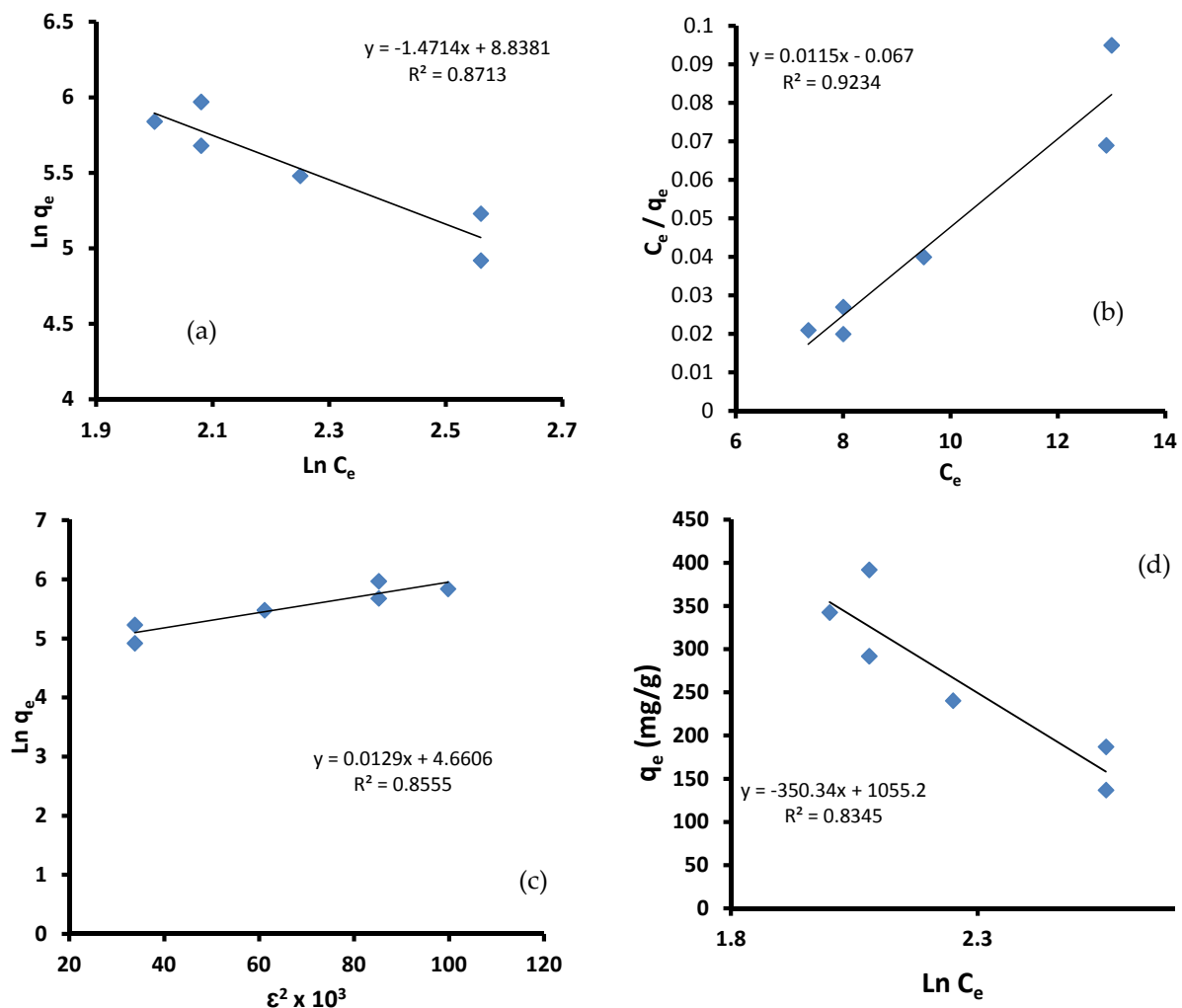| Equilibrium isotherm models			
Langmuir	Freundlich	D–R	Temkin
0.9234	0.8713	0.8555	0.8345

Fig. 9: Sorption isotherm for the Cd(II) ions sorption by BBDP using different isotherm models. (a) Freundlich isotherm, (b) Langmuir isotherm, (c) D-R isotherm, (d) Temkin isotherm.

Table 4
Comparison of the Cd(II) adsorption capacity of different origin activated carbon adsorbents

Adsorbents	Capacity (mg/g)	References
Wood based activated carbon	157.00	[68]
Olive stone activated carbon	11.72	[69]
African palm fruit activated carbon	3,385	[70]
Wheat straw activated carbon	74.63	[71]
Banana bunch activated carbon	87.00	This work

[68–71]. Lloyd-Jones et al. [68] acid oxidised wood based activated carbon, AUG WHK, to enhance its metal binding capacity and subsequently studied for the removal of cadmium ions from aqueous solution. The maximum capacity for the sorbents was 157 mg/g. Alslaibi et al. [69] study, the removal efficiency for cadmium (Cd) from aqueous solution using olive stone activated carbon (OSAC) prepared by microwave. The adsorption isotherm data fitted the Langmuir isotherm well, and the monolayer adsorption capacity was found to be 11.72 mg/g. Abdulrazak et al. [70] study details the removal of heavy metals. Cadmium from wastewater effluent using an activated carbon produced from African palm fruit. The maximum capacity for the sorbents was 3,385 mg/g. Naeem et al. [71] examined novel wheat straw biochar (WSB) and acid treated wheat straw biochar (AWSB) for cadmium removal from contaminated water. Both WSB and AWSB have shown good adsorption capacity of 31.65 and 74.63 mg/g. In our study for removal of Cd(II), the maximum sorption capacity at 25°C was found as 87 mg/g, according to the Langmuir isotherm. It is obvious that the origin of the prepared activated carbon has an impact on the adsorption capacity which correlated directly to the surface area and the porosity characters. However, this comparison is unfair owing to the diversity of the operating conditions and the surface area and the porosity characters of the compared sorbents.

5. Conclusion

The FT-IR, XRD, and SEM analyses showed that the BBDP characterized by the presence of different compounds such as lignin, cellulose, and hemicellulose which mad the BBDP with high porosity to improve the sorption characteristics (pore sizes 10–20 μm). The isotherm experiments conducted at constant temperature showed that the biosorptive capacity of banana bunches were highly dependent on initial pH, initial Cd(II) ion concentration, adsorbent dosage, agitation speed, and time. In this study, the capability of the use of banana bunches were collected from the market for removing Cd(II) was examined. Banana bunches can be easily applied as a cheap biosorbent for Cd(II). This study concluded that BBDP adsorbed the Cd(II) in high efficiency by varying the parameter [98% of Cd(II) after 3 h, optimum pH was 4, the rpm was found to be 150]. The Cd(II) ions removal with BBDP was best described by the Langmuir model and showed a high sorption capacity (87 mg/g) at 25°C. The kinetics of the Cd(II) ions sorption rate was best explained by the pseudo-second-order kinetic equation. According to the *E* values, the sorption process

has a physical nature. The obtained results indicate that the film diffusion is the rate-limiting process.

Acknowledgments

References

[1] Z. Aksu, Biosorption of Heavy Metals by Microalgae in Batch and Continuous Systems, Y.-S. Wong, N.F.Y. Tam, Eds., Algae for Wastewater Treatment, Springer-Verlag and Landes Bioscience, Germany, 1998, p. 37–53.
[2] G. Dönmez, Z. Aksu, The effect of copper(II) ions on growth and bioaccumulation properties of some yeasts, Process Biochem., 35 (1999) 135–142.
[3] N. Babakhouya, S. Boughrara, F. Abad, Kinetics and thermodynamics of Cd(II) ions sorption on mixed sorbents prepared from olive stone and date pit from aqueous solution, Am. J. Environ. Sci., 6 (2010) 470–476.
[4] E. Cheraghi, E. Ameri, A. Moheb, Adsorption of Cd(II) ions from aqueous solutions using sesame as a low-cost biosorbent: kinetics and equilibrium studies, Int. J. Environ. Sci. Technol., 12 (2015) 2579–2592.
[5] J.C. Igwe, A.A. Abia, Adsorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob, Eclet. Quím., 32 (2007) 33–42.
[6] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater., 105 (2003) 121–142.
[7] V. Sameera, N.C.H. Deepthi, S.G. Babu, R.Y. Teja, Role of biosorption in environmental cleanup, J. Microbial. Biochem. Technol., 3 (2011) 1–8.
[8] Z. Aksu, T. Kutsal, A comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*, Environ. Technol., 11 (1990) 979–987.
[9] S.V. Avery, J.M. Tobin, Mechanism of adsorption of hard and soft metal ions to *Saccharomyces cerevisiae* and influence of hard and soft anions, Appl. Environ. Microbiol., 59 (1993) 2851–2856.
[10] G. Dönmez, Z. Aksu, Removal of chromium(VI) from saline wastewaters by *Dunaliella* species, Process Biochem., 38 (2002) 751–762.
[11] S. Abdul-Talib, C.-C. Tay, N.-A. Zakaria, A. Ab-Ghani, L. Mohd-Sidek, N.-W. Chan, Water and environmental engineering: embracing multidisciplinary approach through advanced and integrated technologies for sustainability, J. Asian Sci. Res., 4 (2014) 194–206.
[12] E. Diaz, Microbial Biodegradation: Genomics and Molecular Biology, 1st ed., Caister Academic Press, UK, 2008.
[13] B.S. Inbaraj, K. Selvarani, N. Sulochana, Evaluation of a carbonaceous sorbent prepared from pearl millet husk for its removal of basic dyes, J. Sci. Ind. Res., 61 (2002) 971–978.

[14] S.K. Khare, K.K. Panday, R.M. Srivastava, V.N. Singh, Removal of Victoria blue from aqueous solution by fly ash, J. Chem. Technol. Biotechnol., 38 (1987) 99–104.

[15] I.D. Mall, S.N. Upadhyay, Studies on treatment of basic dyes bearing wastewater by adsorptive treatment using fly ash, Indian J. Environ. Health, 40 (1998) 177–188.

[16] S. Ismadji, S.K. Bhatia, Adsorption of flavour esters on granular activated carbon, Can. J. Chem. Eng., 78 (2000) 892–901.

[17] T. Santhi, S. Manonmani, V.S. Vasantha, Y.T. Chang, A new alternative adsorbent for the removal of cationic dyes from aqueous solution, Arabian J. Chem., 9 (2016) S466–S474.

[18] S. Langergren, Zur theorie der sogenannten adsorption gelöster stoffe, Kungl. Svens. Veternskapsakad. Handl., 24 (1898) 1–39.

[19] Y.S. Ho, G. McKay, The kinetics of sorption of basic dyes from aqueous solutions by sphagnum moss peat, Can. J. Chem. Eng., 76 (1998) 822–826.

[20] M. Ozacar, I.A. Sengil, A kinetic study of metal complex dye sorption onto pinedust, Process Biochem., 40 (2005) 565–572.

[21] G. McKay, M.S. Otterburn, J.A. Aja, Fuller's earth and fired clay as adsorbents for dye stuffs, Water Air Soil Pollut., 24 (1985) 307–322.

[22] W.J. Weber, J.C. Morris, J. Sanity, Kinetics of adsorption on carbon from solution, Eng. Div. Am. Soc. Civ. Eng., 89 (1963) 31–60.

[23] M. Sarkar, P.K. Acharya, B. Bhaskar, Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters, J. Colloid Interface Sci., 266 (2003) 28–32.

[24] G.E. Boyd, A.W. Adamson, I.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites; kinetics, J. Am. Chem. Soc., 69 (1947) 2836–2848.

[25] Y.S. Ho, Effect of pH on lead removal from water using tree fern as the sorbent, Bioresour. Technol., 96 (2005) 1292–1996.

[26] N. Unlu, M. Ersoz, Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbents from aqueous solution, J. Hazard. Mater., 136 (2006) 272–280.

[27] A. Mohammad, A.K.R. Rifaqat, A. Rais, A. Jameel, Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, J. Hazard. Mater., 79 (2000) 117–131.

[28] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination, 225 (2008) 13–28.

[29] A. Seker, T. Shahwan, A.E. Eroglu, Y. Sinan, Z. Demirel, M.C. Dalay, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II), cadmium(II) and nickel(II) ions on *Spirulina platensis*, J. Hazard. Mater., 154 (2008) 973–980.

[30] B.H. Hameed, L.H. Chin, S. Rengaraj, Adsorption of 4-chlorophenol onto activated carbon prepared from rattan sawdust, Desalination, 225 (2008) 185–198.

[31] M.I. Temkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalysts, Acta Physicochim., 12 (1940) 327–356.

[32] WHO, Guidelines for the Safe Use of Wastewater, Excreta and Grey Water, Vol. 1, World Health Organization, 2006, 95 p.

[33] J. Blackwell, P.D. Vasko, J.L. Koenig, Infrared and Raman spectra of the cellulose from the cell wall of *Valonia ventricosa*, J. Appl. Phys., 41 (1970) 4375–4379.

[34] L. Wang, G. Han, Y. Zhang, Comparative study of composition, structure and properties of *Apocynum venetum* fibers under different pretreatments, Carbohydr. Polym., 69 (2007) 391–397.

[35] D.V. Bojić, M.S. Ranđelović, A.R. Zarubica, J.Z. Mitrović, M.D. Radović, M.M. Purenović, A.L. Bojić, Comparison of new biosorbents based on chemically modified *Lagenaria vulgaris* shell, Desal. Water Treat., 51 (2013) 6871–6881.

[36] G. Kirova, Z. Velkova, V. Gochev, Copper(II) removal by heat inactivated *Streptomyces fradiae* biomass: surface chemistry characterization of the biosorbent, J. Biosci. Biotechnol., 2012 (2012) 77–82.

[37] M.S.F. Ramle, O. Sulaiman, R. Hashim, T. Arai, A. Kosugi, H. Abe, Y. Murata, Y. Mori, Characterization of parenchyma and vascular bundle of oil palm trunk as function of storage time, Lignocellulose, 1 (2012) 33–44.

[38] X. Colom, F. Carrillo, Crystallinity changes in lyocell and viscose-type fibers by caustic treatment, Eur. Polym. J., 38 (2002) 2225–2230.

[39] S.J. Kleinübing, R.S. Vieira, M.M. Beppu, E. Guibal, M.G. Carlos da Silva, Characterization and evaluation of copper and nickel biosorption on acidic algae *Sargassum filipendula*, Mater. Res., 13 (2010) 541–550.

[40] H. Liu, F. Yang, Y. Zheng, J. Kang, J. Qu, J.P. Chen, Improvement of metal adsorption onto chitosan/*Sargassum* sp. composite sorbent by an innovative ion-imprint technology, Water Res., 45 (2011) 145–154.

[41] M.O. Kazeem, M.U.K. Shah, A.S. Bahariddin, N.A. Abdul Rahman, Influence of high-pressure steam pretreatment on the structure of rice husk and enzymatic saccharification in a two-step system, Bioresources, 12 (2017) 6207–6236.

[42] W.T. Kwon, D.H. Kim, Y.P. Kim, Characterization of heavy oil fly ash generated from a power plant, AZo J. Mater., 9 (2005) 1–10.

[43] A. Zabaniotou, G. Stavropoulos, V. Skoulou, Activated carbon from olive kernels in a two-stage process: industrial improvement, Bioresour. Technol., 99 (2008) 320–326.

[44] A. Mukherjee, A.R. Zimmerman, W. Harris, Surface chemistry variations among a series of laboratory-produced biochars, Geoderma, 163 (2011) 247–255.

[45] A.M. Dehkhoda, A.H. West, N. Ellis, Biochar based solid acid catalyst for biodiesel production, Appl. Catal., A, 382 (2010) 197–204.

[46] O.A. Mohamad, X. Hao, P. Xie, S. Hatab, Y. Lin, G. Wei, Biosorption of copper(II) from aqueous solution using non-living *Mesorhizobium amorphae* strain CCNWGS0123, Microbes Environ., 27 (2012) 234–241.

[47] Y. Zheng, X. Fang, Z. Ye, Y. Li, W. Cai, Biosorption of Cu(II) on extracellular polymers from *Bacillus* sp. F19, J. Environ. Sci., 20 (2008) 1288–1293.

[48] M. Al-Anber, Removal of iron(III) from model solution using Jordanian natural zeolite: magnetic study, Asian J. Chem., 19 (2007) 3493–3501.

[49] M. Al-Anber, Z. Al-Anber, Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron, Desalination, 255 (2008) 70–81.

[50] R. Malik, S. Lata, S. Singhal, Neem leaf utilization for copper and zinc ions removal from aqueous solution, Int. J. Sci. Res., 3 (2012) 695–705.

[51] P. Somasundaran, S.C. Mehta, X. Yu, S. Krishnakumar, Chapter 6: Colloid Systems and Interfaces Stability of Dispersions Through Polymer and Surfactant Adsorption, K.S. Bird, Ed., Handbook of Surface and Colloid Chemistry, 3rd ed., Taylor & Francis Group, LLC, 2009, pp. 155–194.

[52] H.J. Gong, X.Y. Zhu, K.M. Chen, S.M. Wang, C.L. Zhang, Silicon alleviates oxidative damage of wheat plants in pots under drought, Plant Sci., 169 (2005) 313–321.

[53] K. Vijayaraghavan, K. Palanivelu, M.Velan, Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles, Bioresour. Technol., 97 (2006) 1411–1419.

[54] A.M. Haleem, E.A. Abdulgafoor, The biosorption of Cr(VI) from aqueous solution using date palm fibers (leef), Al-Khwarizmi Eng. J., 6 (2010) 31–36.

[55] Y. Lui, X. Chang, Y. Gue, S. Meng, Biosorption and preconcentration of lead and cadmium on waste Chinese herb Pang DA Hai, J. Hazard. Mater., 135 (2006) 389–394.

[56] H. Li, Y. Lin, W. Guan, J. Chang, L. Xu, J. Guo, G. Wei, Biosorption of Zn(II) by live and dead cells of *Streptomyces ciscaucasicus* strain CCNWHX 72–14, J. Hazard. Mater., 179 (2010) 151–159.

[57] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, A.O. Faruk, Biosorption of chromium(VI) from aqueous solution by cone biomass of *Pinus sylvestris*, Bioresour. Technol., 85 (2002) 155–158.

[58] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[59] R.L. Tseng, Mesopore control of high surface area NaOH-activated carbon, J. Colloid Interface Sci., 303 (2006) 494–502.

[60] F.W. Meng, Study on a Mathematical Model in Predicting Breakthrough Curves of Fixed Bed Adsorption onto Resin

Adsorbent, MS Thesis, Nanjing University, China, 2005, pp. 28–36.

[61] K. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons: a comparative study, Dyes Pigm., 51 (2001) 25–40.

[62] A.E. Ofomaja, Kinetic study and sorption mechanism of methylene blue and methyl violet onto mansonia (*Mansonia altissima*) wood sawdust, Chem. Eng. J., 143 (2008) 85–95.

[63] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, J. Hazard. Mater., 100 (2003) 231–243.

[64] G. Gode, E. Pehlivan, Adsorption of Cr(III) ions by Turkish brown coals, Fuel Process Technol., 86 (2005) 875–884.

[65] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of activated carbons. I investigation of organic vapor adsorption, Zh Fiz Khim, 21 (1947) 1351–1362.

[66] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, Water Air Soil Pollut., 141 (2002) 1–33.

[67] J.M. Smith, Chemical Engineering Kinetics, McGraw-Hill, New York, NY, 1981.

[68] P.J. Lloyd-Jones, J.R. Rangel-Mendez, M. Streat, Sorption of cadmium using a natural biosorbent and activated carbon, IChemE Symp. Ser., 148 (2001) 847–866.

[69] T.M. Alslaibi, I. Abustan, M.A. Ahmad, A. Abu Foul, Cadmium removal from aqueous solution using microwaved olive stone activated carbon, J. Environ. Chem. Eng., 1 (2013) 589–599.

[70] S. Abdulrazak, K. Hussaini, H. M. Sani, Evaluation of removal efficiency of heavy metals by low-cost activated carbon prepared from African palm fruit, Appl. Water Sci., 7 (2017) 3151–3155.

[71] M.A. Naeem, M. Imran, M. Amjad, G. Abbas, M. Tahir, B. Murtaza, A. Zakir, M. Shahid, L. Bulgariu, I. Ahmad, Batch and column scale removal of cadmium from water using raw and acid activated wheat straw biochar, Water, 11 (2019) 1–17.