

Adsorption of Cd^{2+} from synthetic wastewater by modified leaves of *Eupatorium adenophorum* and *Acer oblongum*: thermodynamics, kinetics and equilibrium studies

Hemant Kumar Joshi¹ · Mahesh Chandra Vishwakarma² · Rajesh Kumar³ · Harish Sharma³ · Sushil Kumar Joshi³ · Narendra Singh Bhandari³

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Abstract

Heavy metals cause outrageous ecological risks when released into the environment from many point and non-point sources. Biosorbents prepared from the leaves of *Eupatorium adenophorum* (AEA) and *Acer oblongum* (AAO) were used as practical solutions to remove the toxic heavy metal cadmium (Cd^{2+}) from wastewater. Biosorption of Cd^{2+} was investigated using AEA and AAO biomass under batch conditions. The effect of operating variables like temperature, contact time, the pH impact, and initial metal concentration and biosorbent portion on Cd^{2+} removal has been studied. The optimal pH and the sorbent dosage were found to be 7.0 and 2.0 g L^{-1} , respectively, and removal efficiency attained was 93.3% with an equilibrium removal time of 90 min. The equilibrium uptake of Cd^{2+} was evaluated by Freundlich, Langmuir, and Temkin isotherm models. The Langmuir isotherm model was proved fit confirming single layer of sorption. The biosorption of Cd^{2+} onto activated AEA and AAO biomass achieved were 45.45 mg g^{-1} and 44.64 mg g^{-1} respectively. The adsorption affinity of AEA toward Cd^{2+} was discovered a lot more prominent than AAO biomass. The kinetic data of Cd^{2+} biosorption onto activated AEA and AAO, fitted with a pseudo-second-order well with higher values of R^2 (> 0.99). Thermodynamics disclosed that the adsorption process was spontaneous ($\Delta G^0 < 0$), endothermic ($\Delta H^0 > 0$), and feasible ($\Delta S^0 > 0$). The adsorption of Cd^{2+} onto AEA was more exothermic and spontaneous than the AAO biosorbent. Additionally, FT-IR and SEM analysis uncovered that Cd^{2+} were adsorbed onto selected biomass due to $-\text{NH}-$, $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$ groups. Ionic, coordination bond formation, and electrostatic interaction with Cd^{2+} demonstrated that they were promising biosorbent for wastewater treatment.

Keywords Biosorption · Isotherm · Kinetic study · Thermodynamic study · *Eupatorium adenophorum* (AEA) · *Acer oblongum* (AAO)

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✉ Hemant Kumar Joshi, hemant.as@sitp.ac.in | ¹Department of Chemistry, Nanhi Pari Seemant Engineering Institute, Pithoragarh, Uttarakhand, India. ²Department of Chemistry, K.K. Pt. B.D. Pandey Govt. Post Graduate College, SSJ University, Almora, Bageshwar, Uttarakhand, India. ³Department of Chemistry, SSJ University, SSJ Campus, Almora, Uttarakhand, India.



1 Introduction

Heavy metals threaten human wellbeing and pollute the environment. There has been a disturbing expansion in biological and overall health concerns associated with natural contamination by these metals. Expanding industrialization, for example, fertilizer sectors, alloy manufacturing, mining operations, paper industries, batteries, pigments, tanneries, refining processes, metal plating facilities, pesticides, and pigments, and so forth, contains a high concentration of metals, which are released into the environment straightforwardly or in a roundabout way in many developing countries [1–3].

Unlike organic pollutants, heavy metals like cadmium are not capable to decompose and tend to lump in the life cycle of living organisms. The toxic metal cadmium discharges into wastewater from the electroplating industry, nickel–cadmium batteries, fertilizers, pesticides, dyes, and textile operations [4, 5]. Cadmium can cause many disorders like respiratory cancers (lung carcinoma), renal disturbances, lung cancer, hypertension, and bone lesions in humans [2]. The toxic nature of cadmium is recognized by the United States Environmental Protection Agency, which classifies it as a “priority pollutant” and limits effluents and consumable water to 0.1 and 0.05 mg L⁻¹, respectively [4, 6]. Thusly, it is essentially important to develop low-cost and effective technologies for the removal and recovery of heavy metals from wastewaters before their release into the environment.

Some traditional techniques, such as precipitation or ion exchange methods, are not helpful in removing cadmium from wastewater when the concentration range is high. The use of biomass as biosorbents for heavy metal removal may be a viable alternative to the existing methods [7]. Heavy metals are adsorbed by vacuoles of chemically treated biomass by ionic, coordination bond formation, and electrostatic interactions from wastewater. Adsorption is one of the common, cost-effective, safest, and easiest techniques to eliminate heavy metals from wastewater and it can be utilized for environmental remediation [8]. Various kinds of chemical and bio-based materials, like activated carbon [3, 9, 10], inorganic minerals [11], biomass [1, 4, 5, 12–43], and polymers [6, 44–49], are utilized as adsorbents to remove metal ion from wastewater. The metal adsorption capacity of adsorbents is mainly controlled by the active sites of its surface, which may incorporate functional groups such as C=O, O–H, –NH₂, and –SO₃H. Physical and chemical interactions are mainly responsible for the attachment of metal ions to the surface of adsorbents. These interactions and techniques are the combined process of coordination interaction, ion-exchange process, complexation, electrostatic interactions, micro precipitation, and redox reactions [7, 8, 12, 14, 16, 17, 19, 22, 23, 27, 34, 36–40, 50, 51].

Regular physicochemical technique such as chemical oxidation or reduction, precipitation, evaporation, electrodialysis, ion exchange, and liquid–liquid extraction has been advanced with time. These methods are incredibly expensive or ineffective when the metal concentration focus scope of particles is 1 to 100 mg L⁻¹. Subsequently, it is necessary to develop new strategies for the metal expulsion from the effluents before releasing them into the general environment [12, 14, 16, 19, 22, 23, 34–36, 39, 51–53].

However, exceptionally proficient, minimal effort, effectively accessible, simple to recover, and eco-accommodating adsorbent is extremely important for the handling of a lot of wastewater. Squander plant biomass, as an adsorbent, is plentifully and unreservedly accessible in the thick woods zone [1, 4, 5, 11, 12, 14–23, 25–28, 34–36, 39, 50–61]. In this manner, squander plant biomass, as an inexhaustible characteristic asset, for example, *Aesculusindica seed shell* [20], *Shewanellaputrefaciens* [4], *Amanita rubescens* [43], coffee grounds [34], vegetable waste [27], *Rubusellipticus* [14] are utilized as an adsorbent for Cd²⁺ particle expulsion from wastewater.

In this study, plant leaves of *Eupatorium adenophorum* (AEA) and *Acer oblongum* (AAO) biomass is chemically treated for the synthesis of biosorbent. Biosorbent is employed in the removal of Cd²⁺ from synthetic wastewater. The characteristics of the biomass such as the surface conduct and functional group are studied using Scanning Electronic Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR) analysis. The effect of operating variables like initial pH, contact time, biosorbent dosage, temperature and initial metal ion concentration on the Cd²⁺ are evaluated using AEA and AAO. Parameters such as the biosorption capacity, removal efficiency and biosorption pathway of the cadmium metal ion (Cd²⁺) are determined by equilibration studies. The mechanism of metal removal is investigated through adsorption isotherm, thermodynamics and kinetics studies. Desorption and reusability studies of AEA and AAO biomass are also performed for the compelling adsorption of Cd²⁺ in synthetic wastewater.

2 Materials and methods

2.1 Preparation of adsorbent

Plant leaves of *Eupatorium adenophorum* (AEA) and *Acer oblongum* (AAO) biomass were gathered from the edges of town Almora, and high height territories of Chopta, Rudraprayag Uttarakhand, India. To eliminate dissolvable materials and residue, these were washed with double-distilled water, desiccated at room temperature 24 h and then placed at 60 °C in an oven (Model: SN-1680, Popular Trader). In an electric processor, the dried biomass is crushed into a fine powder. In order to protonate, the powdered biomass was soaked in acid (0.1 N HNO₃) for 24 h, at room temperature. The biomass was then washed in double distilled water and dried at 60 °C overnight. About 15% reduction in weight was observed. It was then grounded and sieved to get an average particle size of 250 Mesh and afterward kept in an impenetrable bottle, which will be used as an adsorbent later on.

FTIR spectroscopy was used to detect surface functional groups of the treated adsorbent (Model: spectrum 10 version, PerkinElmer) and JEOL-JSM6610-JFC1600 model was used for Scanning Electronic Microscopy (SEM).

2.2 Preparation of adsorbate

The quality of the reagents used was analytical reagent grade. The stock arrangement (1000 mg L⁻¹) of the Cadmium chloride (CdCl₂) was set up in double-distilled water. The earlier literature [53] revealed that the pH value of industrial effluent was somewhere in the range 4–5, so the pH of the prepared solutions was adjusted to 5 using 0.1 N NaOH or 0.1 N HCl solutions, which was further checked by a Digital pH meter (Model: Systronic 361). The scope of cadmium particle concentration in synthetic wastewater ranged between 10 and 50 mg L⁻¹.

2.3 Biosorption experiments

The biosorption was handled with the planning of 100 mL of standard arrangement in a 250 mL Erlenmeyer flask (Borosil). Further, solutions were shaken at 170 rpm for 30 min and simply filtered with Whatman filter paper of 11 µm particle retention. The filtrate was processed with concentrated HNO₃ and studied by Atomic Absorption Spectrophotometer (Model: Optima 4300 DV ICP, PerkinElmer, Boston, MA). Each investigation was repeated two times for more accurate results. The adsorption of Cd²⁺ particles was studied within the 1.0–9.0 pH range. The measured mass of added adsorbent and initial concentration of Cd²⁺ ion was 1.0 g and 10 mg L⁻¹, respectively [32, 58]. Besides, the effect of dosage mass of adsorbents on the wastewater of Cd²⁺ particles was studied by changing its quantities from 0.5 to 2.5 g (in the multiples of 0.5 g) at 170 rpm for 30 min.

At equilibrium, the adsorption proficiency of the adsorbent and quantity of adsorbed metal (q_e) with the unit mg g⁻¹ to create the variable for adsorption efficiency was determined by Eq. 1 and Eq. 2 respectively.

$$\text{Adsorption efficiency} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$\text{Quantity of metal adsorbed } (q_e) = \frac{(C_i - C_e) \times V}{m} \quad (2)$$

where C_i and C_e are the initial and final concentrations of metal ions, in mg L⁻¹, respectively. V is the volume of solution in Liter; m is the mass of biosorbent in grams.

2.4 Thermodynamic study of biosorption

The Gibbs standard free energy change (ΔG^0) could be calculated by Eq. 3.

$$\Delta G^0 = -RT \times \ln K_c \quad (3)$$

where R was the gas constant with the value $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T was the absolute temperature in Kelvin, and K_C was the adsorption partition coefficient (l mg^{-1}) of biosorption, which was calculated by Eq. 4.

$$K_C = \frac{C_{Ae}}{C_e} \quad (4)$$

where C_e was the equilibrium adsorption capacity (mmol g^{-1}) and C_{Ae} was the equilibrium concentration (mmol L^{-1}) were the metal ions concentration of the solution in equilibrium and equilibrium adsorption of metal ions, respectively.

The relation of ΔG^0 with the standard enthalpy change ΔH^0 (kJ mol^{-1}) and standard entropy ΔS^0 ($\text{J mol}^{-1} \text{ K}^{-1}$) of the adsorption process are shown in Eq. 5.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (5)$$

The values of ΔH^0 and ΔS^0 were calculated with the assistance of the intercept and slope of the Van't Hoff plot ($\ln K_C$ versus $1/T$) (Eq. 6).

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

2.5 Adsorption isotherms

The non-linear form of the Langmuir model and its linear form could be expressed in Eqs. 7 and 8, respectively [62].

$$Q_e = \frac{K_L Q_{\max} C_e}{1 + K_L C_e}, \quad (7)$$

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}}, \quad (8)$$

where Q_e and C_e were adsorption capacity at equilibrium and concentration of metal at equilibrium, respectively. $Q_{\max}$ could be expressed as monolayer adsorption capacity of the absorbent.

The Freundlich model and its empirical form were given as Eq. 9 and 10, based on the adsorption of Cd^{2+} ions on heterogeneous sites and multilayer biosorption [63].

$$Q_e = K_F C_e^{\frac{1}{n}}, \quad (9)$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e, \quad (10)$$

where K_F , a constant, is related to the adsorption efficiency and n is related to the adsorption amplitude of the biosorbent.

The Temkin isotherm model was given in Eq. 11:

$$q_e = B_T \ln A + B_T \ln C_e, \quad (11)$$

where $B_T = \frac{R \times T}{b_T}$; T is the absolute temperature (K) and R is the gas constant ($\text{J K}^{-1} \text{ mol}^{-1}$), the constant b_T is the heat of adsorption (J mole^{-1}), A is the equilibrium binding constant (L gm^{-1}), C_e concentration of the adsorbate (mg L^{-1}), q_e is the amount of metal adsorbed (mg g^{-1}). The values of b_T and K_T were recorded by a linear plot of q_e versus $\ln C_e$ using slope and intercept.

2.6 Biosorption kinetics

The Eq. 12 demonstrates the pseudo-first-order kinetic model.

$$\ln (q_e - q_t) = \ln q_e - k_1 t, \quad (12)$$

where q_e and q_t are the amounts of adsorbed metal ion (mg g^{-1}) at equilibrium, and at time t (min) respectively and K_1 is the pseudo-first-order adsorption rate constant (min^{-1}).

The linear form articulation for pseudo-second-order kinetics was determined by Eq. 13.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (13)$$

where k_2 is the pseudo second-order model adsorption rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$), q_e is the amount of adsorption capacity (mg g^{-1}), q_t is the capacity of adsorption at time t (mg g^{-1}), and t is the adsorption time (min).

2.7 Desorption experiment

Desorption experiments were performed using a 100 ml conical flask containing the eluent solution. 500 mg of cadmium-loaded biomass was suspended in a flask containing the eluent solution. The mixture was stirred at 170 rpm at 250 °C for 45 min. The biosorbent was separated by filtering the solution using Whatman 42 filter paper. The total Cd^{2+} metal ion concentration in the desorption solution was determined by atomic absorption spectroscopy (AAS) and desorption capacity (q_e , desorption mg g^{-1}) was calculated using the following equation:

$$q_{e(\text{desorption})} = \frac{V_d \times C_{ed}}{m_d}, \quad (14)$$

where C_{ed} is the Cd^{2+} metal ions concentration in a desorption solution (mg l^{-1}), V_d is the volume of desorption solution (l) and m_d is the mass of metal-loaded biosorbent (g). The percentage of Cd^{2+} metal ions desorbed from the loaded biomass was calculated as follows:

$$\text{Desorption}(\%) = \frac{q_{e(\text{desorption})}}{q_{e(\text{biosorption})}}. \quad (15)$$

To investigate the adsorption capacity of Cd^{2+} from AEA and AAO, only 0.5 g of adsorbent was dispersed in 100 ml de-ionized water in a separate flask. The pH value of the solution was adjusted by adding HNO_3 . Finally, equilibrium was achieved and the Cd^{2+} particle concentration and desorption results were recorded.

3 Results and discussion

3.1 Characterization of modified AEA and AAO

3.1.1 FT-IR analysis

The FT-IR study revealed that many functional groups were present in AEA and AAO biomass. This examination gave data about conceivable cell-metal particle interactions between functional groups of biosorbent and Cd^{2+} . To investigate the cooperation of AEA and AAO with metal particles, spectra were recorded during biosorption (Fig. 1). It can be noticed from the FT-IR spectra that the transmittance of peaks in the Cd^{2+} -ion-loaded AEA and AAO biomass is lower than that of the unloaded [20].

As shown in Fig. 1a, the FT-IR spectra of AEA and AEA- Cd^{2+} ion, the sharp peak around 3742 cm^{-1} is a common companion to hydroxyl peaks, it represents the non-hydrogen bonded O–H group. The absorption band in the region of 2916 cm^{-1} and 2848 cm^{-1} are characteristic of the C–H group, while after adsorption of Cd^{2+} , the peak gone through to a countable change in the intensity and the wave number [2].

The bands appearing in the region 1611 cm^{-1} and 1516 cm^{-1} might be attributed to $>\text{C}=\text{N}$, $>\text{C}=\text{C}<$, and $>\text{C}=\text{O}$ stretch whereas in the region 1438 cm^{-1} might represent C–O stretching of COO group responsible for Cd^{2+} -oxygen complex formation. The presence of cellulose and hemicellulose in plant materials may give –OH, $>\text{C}=\text{O}$, and $-\text{NH}_2$ groups. Figure 1 shows their absorption peaks, which could be responsible for Cd^{2+} ion removal from aqueous systems [5].

The peaks at 1611 , 1516 , 1438 , 1030 and 638 cm^{-1} are moved to 1650 , 1523 , 1458 , 1025 and 647 cm^{-1} respectively. This decrease in the adsorption band of C–O, was observed due to the complex formation of oxygen atoms and Cd^{2+} .

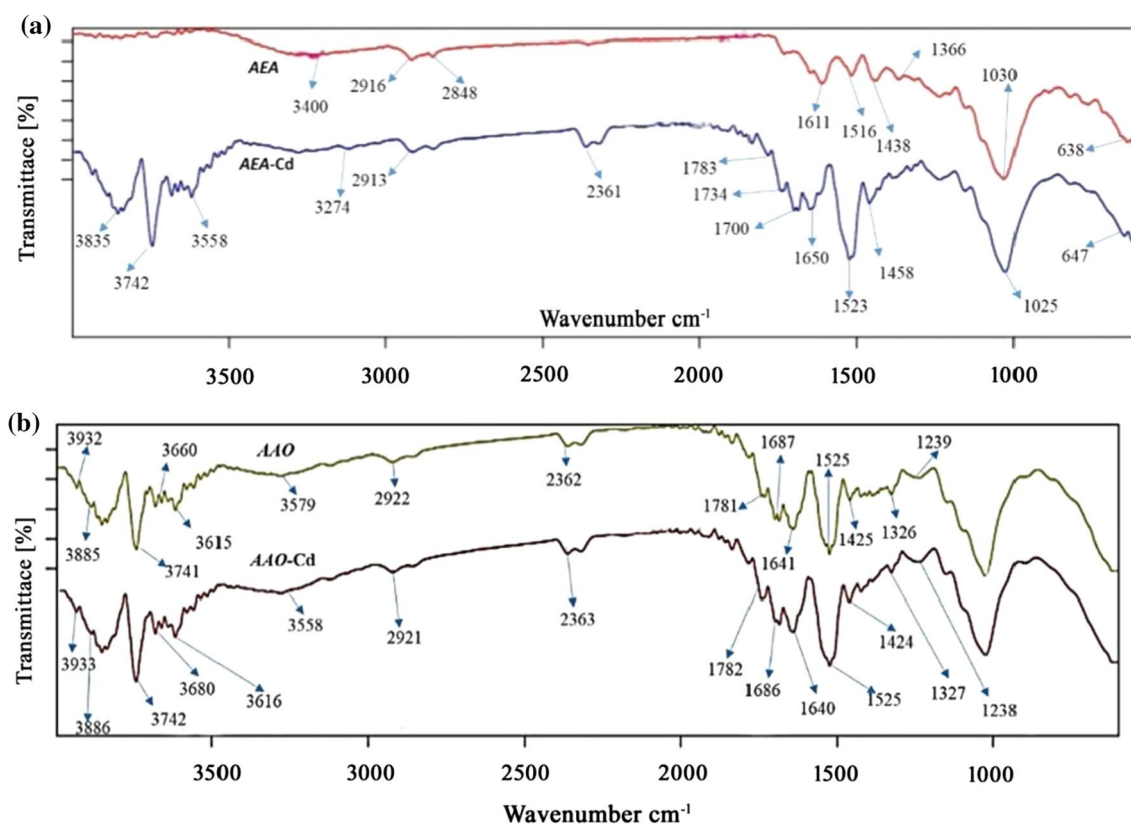


Fig. 1 FT-IR spectra of Cd^{2+} ion loaded and unloaded with (a) AEA (b) AAO biomass

ions [43]. While after adsorption of metal ions, $-\text{CH}_2-\text{O}-\text{CH}_2-$ linkage arose at $1030\text{--}1104\text{ cm}^{-1}$ [27, 34, 35]. These movements, on account of the arrangement of the complex compound, demonstrated that Cd^{2+} ions were effectively adsorbed on AEA [14, 27, 43]. It is concluded that the AEA includes oxygen-containing functional groups that provide additional active sites in the adsorption process.

In Fig. 1b, the adsorption band at 3932, 3885, 3741, 3660, 3615, and 3579 cm^{-1} of AAO were noticed, which may be a direct result of extending the vibration band of N–H, carboxylic, hydroxyl, and $-\text{NH}_2$ groups [14]. It is evident from this figure that the characteristic absorption peak of O–H and N–H stretching vibration was shifted from 3660 to 3680 and 3579 to 3558 cm^{-1} respectively. Which shows the change in the free hydroxyl and primary amine group content due to the interaction between Cd^{2+}/OH and $\text{Cd}^{2+}/\text{N-H}$ groups of the adsorbent. The peak at 1525, 1425, and 1326 cm^{-1} were identified with saccharide structure, which was liable for C–O, C–O–H, and C–C bending vibration [4]. After successful sorption of cadmium ion, these absorption bands were shifted towards other wavenumbers. These results also indicate that chemisorption could also be involved in the adsorption of cadmium metal ions onto AEA and AAO.

3.1.2 Scanning electronic microscopy analysis

Scanning Electronic Microscopy (SEM) technique was executed for the examination of surface and texture morphology, porosity, and properties of bio adsorbent [12, 23, 39, 50, 51]. The morphology of the activated AEA, AAO, AEA-Cd, and AAO-Cd was observed, shown in Fig. 2. The surface of AEA-Cd and AAO-Cd was different from AEA and AAO, the area for Cd^{2+} interaction and surface became smooth with the Cd^{2+} attached to the surface [5].

As shown in Fig. 2a and c, the crude biosorbent has a rough, uneven surface and a rigid structure. Additionally, it is noted that cavitations and pore differ in size. According to this indication, sorbents can be used for adsorption. As can be seen in Fig. 2b and d, the surface transition becomes smooth and swollen after cadmium adsorption. This suggests that the metal has adhered to the biosorbent.

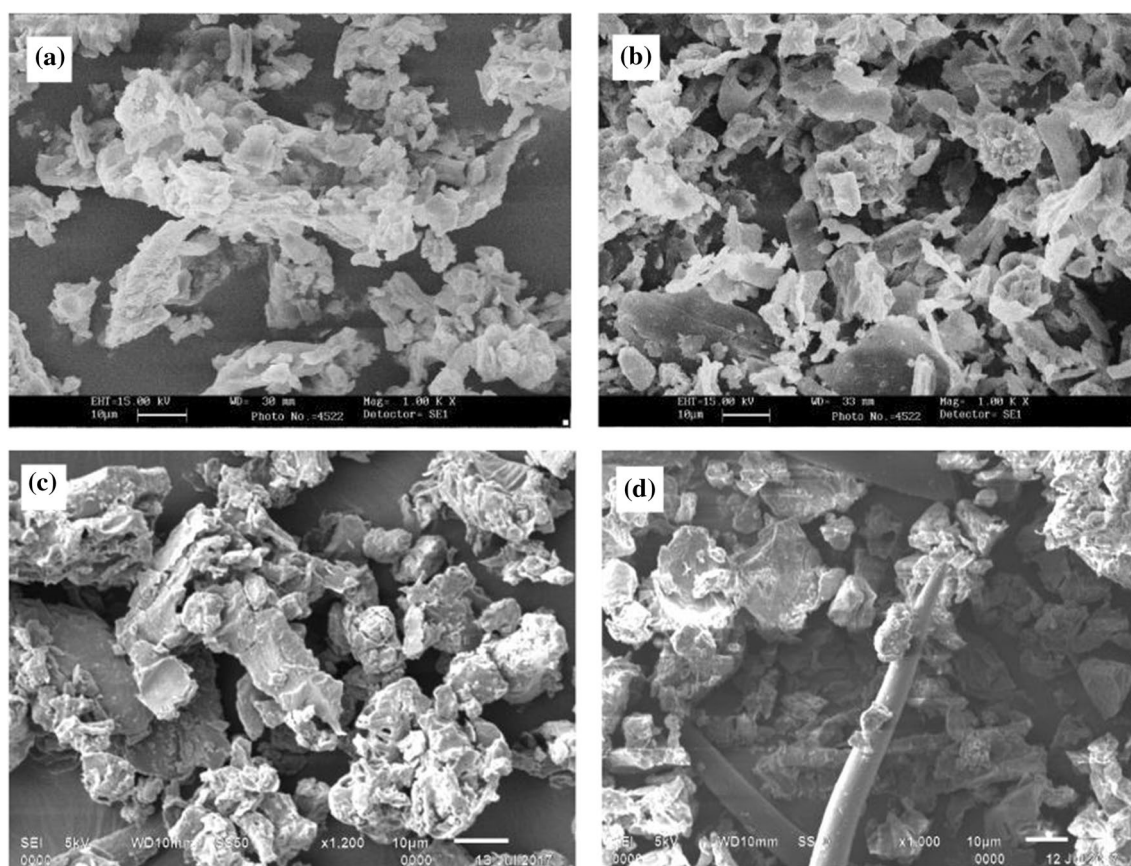


Fig. 2 SEM image of **a** AEA; **b** AEA-Cd; **c** AAO; **d** AAO-Cd

3.2 Effect on Cd^{2+} equilibrium adsorption

3.2.1 The pH effect

The pH value presents consequences for the surface charge of biosorbent, the level of ionization of the metal, and metal particle dissolvability in the biosorption phenomenon [17]. The removal proficiency of Cd^{2+} ions with activated AEA biomass was 7.5, 27.7, 80, and 88.9% (which is achieved greatest) at pH 1, 3, 5, and 7, respectively (Additional file 1, Fig. S1). While the removal percentage observed decreasing with expanding pH from 7 to 9 and it reached 70.2% at pH 9. Furthermore, with activated AAO biomass, the removal efficiency of Cd^{2+} ions was recorded 36, 60, 85, and 96% (expanded quickly) at pH 1, 3, 5, and 7 respectively. On expanding pH from 7 to 9 the removal percentage diminishes to 79%.

The data revealed that the percentage removal of the metal ions onto activated biomass increases with an increase in pH from 1 to 7, decreasing after pH 7. However, it was likewise presumed that the activated AAO biomass is more efficient than activated AEA at an ideal level of pH 7.0.

The minimum biosorption of Cd^{2+} ions at pH 1 was recorded which can be ascribed that the protonation of the dynamic sites of the biosorbent at low pH (< 7). Decreasing biosorption is caused because of the repulsion between metal particles and the H^+ particle [60]. Also, Cd^{2+} ions upgraded competition for biosorption and ion-exchange sites with protons at low pH [15, 16]. The other explanation behind this conduct could be the binding of H^+ to the functional groups of biomass. Which actuated an electrostatic repulsion between metal particles and dynamic locales of the adsorbent [19].

Generally, metal biosorption included adsorption by physical forces, complex mechanisms of ion-exchange, chelation, and ion entrapment of the biosorbent sites [17]. At a pH more noteworthy than 7 the biosorbent is deprotonated and makes more dynamic sites. There is a decrease in the removal efficiency as the pH increments from 7 to 9 might be credited to the arrangement of metal hydroxide at exceptionally high pH (> 7) [40]. Thusly, at high pH (> 7) Cd^{2+} ion get precipitated into hydroxide compound ($\text{Cd}(\text{OH})_2$) [15, 50].

3.2.2 Effect of biosorbent dose

The impact of the adsorbent portion on the removal percentage of Cd^{2+} ions was examined (Additional file 1, Fig. S2). As appeared in Additional file 1, Fig. S2, removal efficient percentage of Cd^{2+} ions, was accomplished 60, 87, and 85% onto AEA and it was 66, 90, and 87% onto AAO biomass for 0.5, 2.0, and 2.5 g biosorbent doses respectively. It was also observed that the adsorption capacity was decreased when the biosorbent dose was increased from 0.5 to 2.0 g for both biosorbent. The range of decreased values was 1.2 to 0.3 mg g^{-1} for AEA and 1.3 to 0.3 mg g^{-1} for AAO.

The analysis revealed that an expansion in the portion of biosorbent from 0.5 to 2 g, the removal efficiency increases, and adsorption capacity decreases, yet after 2 g of biosorbent dose removal percentage diminished for both AEA and AAO. This variation may comprise two reasons: initially, inoccupation of the adsorption sites, which may cause due by an expansion in biosorbent area, at constant metal particle concentration, and a steady volume. Furthermore, high particulate cooperation likes as collection because of high biosorbent measurements [17]. After the attainment of equilibrium, between biosorbent surface and metal ions, further adsorption of Cd^{2+} ion was not observed [37]. The outcome showed that the activated AAO had better adsorption capacity when contrasted with AEA and could be considered a promising adsorbent (Additional file 1, Fig. S3).

3.2.3 The effect of initial concentration

The impact of the initial Cd^{2+} concentration ion in the adsorption process was recorded (Additional file 1, Fig. S2). For Cd^{2+} ion onto the activated AEA biomass, the removal efficiency was found 79.00, 70.33, and 60.40% in 10, 30, and 50 mg L^{-1} of Cd^{2+} ion concentration respectively. The maximum removal efficiency of 81, 78, 68, and 61% for Cd^{2+} ion onto the activated AAO biomass is accomplished at 10, 20, 40, and 50 mg L^{-1} of metal ion concentration. The examination inferred that the removal efficiency (%) of Cd^{2+} ions diminished with the expansion of the underlying fixation. This may be a result of the way that, for a given portion of adsorbent the absolute number of accessible adsorption locales was fixed [27].

The greatest biosorption effectiveness was recorded at the convergence of 10 mg L^{-1} . In any case, simultaneously, the equilibrium adsorption of Cd^{2+} ions expanded from 0.79 to 3.02 mg g^{-1} with the expansion of metal ion concentration from 10 to 50 mg L^{-1} per unit of adsorbent AEA. Biosorption capacity increased from 0.81 to 3.09 mg g^{-1} , and high biosorption capacity was recorded at 50 mg L^{-1} of metal ion concentration for AAO adsorbent. This might be due to an increasing concentration gradient which acts as an increasing driving force to overcome the resistance to mass transfer of metal ions between the aqueous phase and the solid phase [38].

3.2.4 Effect of contact time of adsorption

The impact of adsorption holding time on the adsorption of Cd^{2+} ions onto AEA and AAO biomass was explored at numerous concentrations. The contact time of adsorption of Cd^{2+} ions with 1 g per 100 mL of biosorbent was ranged from 15 to 105 min. The concentration of Cd^{2+} ions solution was prepared at 10, 30, and 50 mg L^{-1} at a constant shaking speed of 170 rpm. As shown in Additional file 1, Fig. S3, when the concentration of Cd^{2+} ions was 10 mg L^{-1} , the removal percentage was found 60, 83, 90, and 93.3% for AAO with a contact time of 15, 30, 45, and 75 min respectively and it was 60, 81, 87 and 91.1% for AEA with same time interval.

When the concentration was kept at 30 mg L^{-1} Cd^{2+} ions, the removal percentage achieved was 56.66, 80.36, 80.84, and 82.96% for AEA with a contact time of 15, 30, 45, and 75 min, respectively. And it was 40, 70.33, 77.33%, and 83% for AAO with the same contact time (Additional file 1, Fig. S3). When contacting time was increased from 15 to 90 min the removal percent gradually increased from 56.67 to 83.34% for AEA biosorbent and the following hour and a half biosorption was found to be almost in equilibrium. The removal percent was measured when contact time changed from 15 to 105 min with biosorbent AAO. The removal percentage gets increased from 56.67 to 83.34% in 15 min to 90 min.

The removal percentage accomplished for 50 mg L^{-1} of Cd^{2+} ion onto AEA biomass was 45.94, 70.12, 70.96, and 73.16% with a contact time of 15, 30, 45, and 75 min respectively. For AAO biomass, it was 25.2, 61.8, 69.8, and 60% during the same time intervals, respectively (Additional file 1, Fig. S3). For activated AEA and AAO biomass, after 30 and 105 min, it expanded step by step to 74% and 80% respectively.

This proposes that the adsorption capacity and percentage removal efficiency increments significantly with time, which came to equilibrium under 90 min interval time. However, following an hour and a half, the surface sites of

biosorbent might be occupied and the Cd^{2+} ion may require additional main thrust for more adsorption of the adsorbent sites after equilibrium [31, 43]. The capacity of adsorption of AEA and AAO, expanded with an expansion in initial Cd^{2+} ion concentration, while the percentage removal of Cd^{2+} ion indicated a contrary pattern.

3.2.5 The effect of temperature

The outcome demonstrated that the removal efficiency of Cd^{2+} ion was 40, 82, 91, and 69.9% at the reaction temperature 288, 303, 318, 333, and 348 K respectively with AEA biosorbent. As shown in Additional file 1, Fig. S4, the removal percent was 50, 69, 89.9, and 51% at 288, 303, 333, and 348 K with AAO biosorbent. In both cases, something regular was noticed, at first upon the expansion of temperature, it increments; however at high temperature (at 348 K) it unexpectedly diminishes.

This conduct may be because of the accessibility of active adsorbent sites. The pore size gets broader and it can support to commencement order of biosorbent [43]. To plan a biosorbent for future biosorption attempts the ideal temperature should 318 K for AEA and 333 K for AAO. Additionally, it may in like manner be contemplated that AAO is more proficient when differentiated to AEA biosorbent at high temperatures for 10 mg L^{-1} of Cd^{2+} particles.

3.2.6 Thermodynamic study of biosorption

The adsorption process was analyzed by thermodynamic theory. The thermodynamic parameters were calculated by Eq. 3–6 and values are shown in Table 1. The values of ΔH^0 and ΔS^0 were calculated with the assistance of the intercept and slope of the Van't Hoff plot ($\ln K_c$ versus $1/T$) (Eq. 6). As shown in Table 1, the K_c values decreased with an increase in temperature, resulting in a shift of equilibrium to the left i.e. desorption of the adsorbed metal ions was favored at higher temperatures. The positive values of ΔH^0 and negative values of ΔG^0 suggest the endothermic nature and the spontaneous nature of the adsorption process, respectively.

The low enthalpy values of ΔH^0 (20 kJ mol^{-1}) indicate that physical sorption is involved in the process of adsorption [22, 25, 43]. The estimated values of ΔH^0 were recorded more than 20 kJ mol^{-1} for AEA biomass (Table 1). Hence, the sorption mechanism may involve chemisorption. But these values were found less than 20 kJ mol^{-1} for AAO biomass; the process for it may be a spontaneous sorption mechanism, as ion exchange.

The values of ΔS^0 reports adsorbent and adsorbate affinity for AEA and AAO recorded were 130.22 and $+238.99 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively, which may be because of underlying changes in the adsorbate and biosorbents. The positive value of ΔS^0 shown in Table 1 illustrates that the adsorbent process was endothermic. The positive value of ΔS^0 consistently calls attention to the improving haphazardness at the strong fluid interface [31, 41].

As appeared in Table 1, the ΔG^0 values were negative with increased values 0.971 to -6.117 from 288 to 318 K for AEA and 0 to -6.053 from 288 to 333 K for AAO. It meant that the expansion in spontaneity and feasibility with its ascent in temperature up to 318 K.

After 318 K the free energy change was decreased which decreases the spontaneity of the biosorption process. The ΔG^0 values were found to be positive at 348 K and become more negative at 333 K. This demonstrated the diminishing in spontaneity with increasing temperature, which was additionally associated with the endothermic reaction. For physical and chemical adsorption, ΔG^0 ranges from -20 to 0 kJ mol^{-1} and -80 to -400 kJ mol^{-1} , respectively [26].

3.2.7 Linear and nonlinear adsorption isotherms

The equilibrium data of adsorption of Cd^{2+} ion onto AEA and AAO were tested linearly and non-linearly with three models, Langmuir, Freundlich, and Temkin. The Langmuir model and its linear form could be expressed in Eq. 7 and

Table 1 Thermodynamic parameters for adsorption of Cd^{2+} onto activated AEA and AAO biosorbent

Temperature (K)	AEA				AAO			
	$\Delta G^0 (\text{kJ mol}^{-1})$	K_c	$\Delta H^0 (\text{kJ mol}^{-1})$	$\Delta S^0 (\text{J K}^{-1} \text{ mol}^{-1})$	$\Delta G^0 (\text{kJ mol}^{-1})$	K_c	$\Delta H^0 (\text{kJ mol}^{-1})$	$\Delta S^0 (\text{J K}^{-1} \text{ mol}^{-1})$
288	0.971	1.22	+37.57	+130.22	0.000	1	+69.43	+238.99
303	-3.820	3.76			-2.016	2.22		
318	-6.117	10.11			-3.503	4.26		
333					-6.053	8.90		

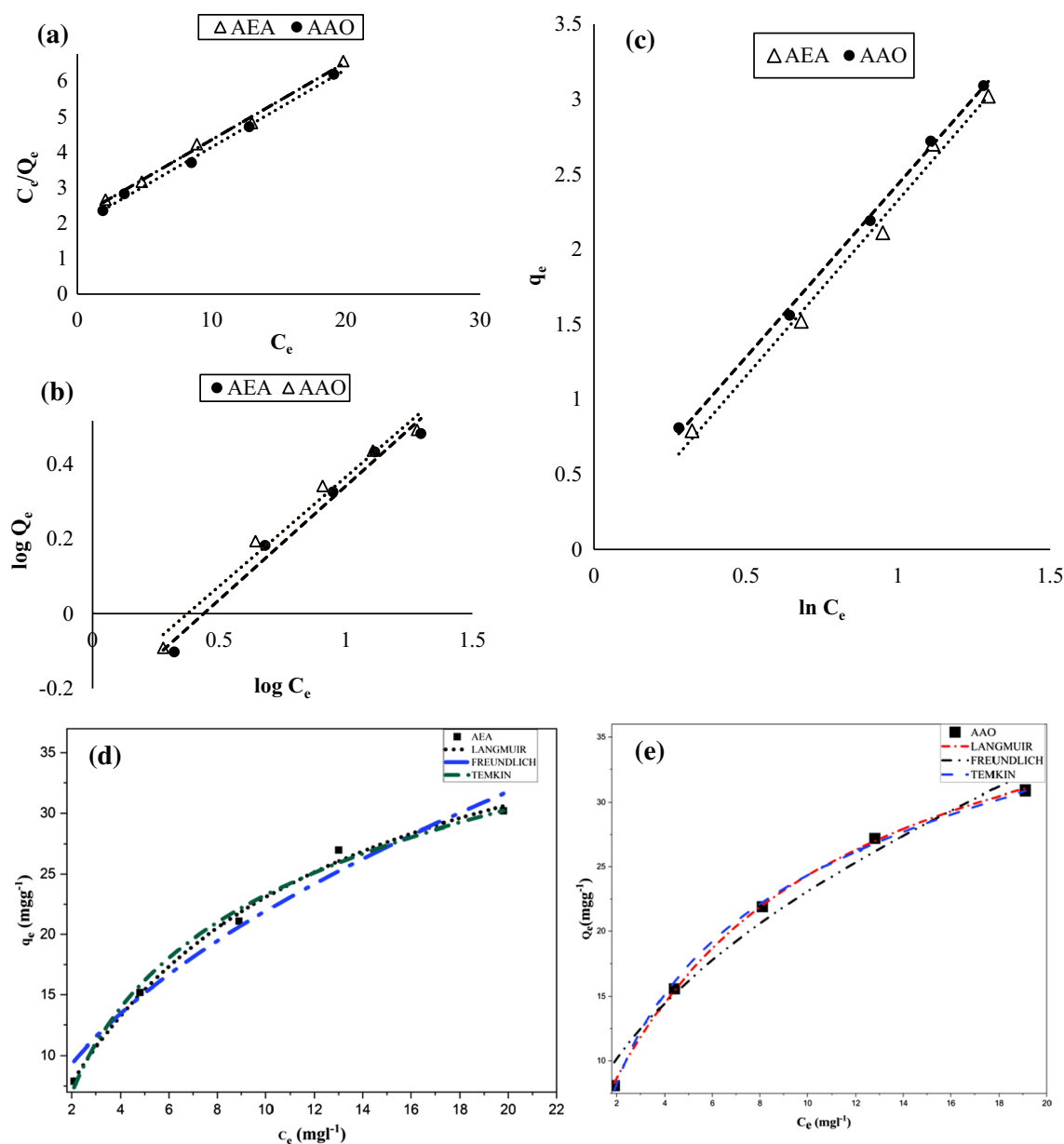


Fig. 3 Linear isotherm model for biosorption of Cd²⁺ onto activated AEA and AAO biomass **a** Langmuir isotherm, **b** Freundlich isotherm, **c** Temkin isotherm, **d** nonlinear isotherm models for AEA, **e** nonlinear isotherm models for AAO

8, respectively [64]. The values of Langmuir parameters $Q_{\max}$ and K_L were evaluated from the linear plot of C_e/Q_e versus C_e (Fig. 3a) and non-linear plot (Fig. 3d, e). The values of $Q_{\max}$, K_L , and correlation coefficient R^2 were displayed in Table 2. The plot investigation showed that the Langmuir equation was fitted with the adsorption data. The regression coefficient R^2 for linear Langmuir isotherm was recorded as 0.994 and 0.997 and for non-linear Langmuir isotherm was recorded 0.995 and 0.999 for AEA and AAO, respectively. The AAO and AEA have almost the same adsorption capacity, $Q_{\max}$, and it was 44.64 mg g⁻¹ and 45.45 mg g⁻¹ for linear isotherm and 44.44 mg g⁻¹ and 45.77 for non-linear isotherm, respectively.

The Freundlich model and its empirical form were given as Eq. 9 and 10, based on the adsorption of Cd²⁺ ions on heterogeneous sites and multilayer biosorption [63]. The value of K_F and $1/n$ was determined with the help of the linear plot ($\log Q_e$ versus $\log C_e$) i.e. by slope and intercept (Fig. 3b), the Freundlich isotherms outlined for the straight plots. K_F and n values were recorded 0.542 and 0.607 on to AEA; 0.605 and 1.715 onto AAO for Cd²⁺ ion. For non-linear model K_F and n values were recorded 6.4 and 0.534 on to AEA; 7.123 and 0.51 onto AAO for Cd²⁺ ion (Fig. 3d, e).

Table 2 Biosorption isotherm constants for sorption of Cd^{2+} onto activated AEA and AAO biomass

Biosorbent	Isotherm model	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
		$Q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2	b_T (mg g^{-1})	A	R^2
AEA	Non-linear	45.77	0.102	0.995	6.4	0.534	0.974	10.17	0.983	0.991
	Linear	45.45	0.101	0.994	0.542	0.607	0.979	2.344	0.992	0.990
AAO	Non-linear	44.44	0.121	0.999	7.123	0.51	0.978	10.01	1.137	0.997
	Linear	44.64	0.112	0.997	0.605	1.715	0.977	2.306	1.057	0.997

Table 3 The standard error values for biosorption of Cd^{2+} with AEA and AAO biomass

Biosorbent	AEA						AAO					
	Langmuir		Temkin		Freundlich		Langmuir		Temkin		Freundlich	
Parameters	K_L	$Q_{\max}$	A	b_T	K_F (mg g^{-1})	n	K_L	$Q_{\max}$	A	b_T	K_F (mg g^{-1})	n
Values	0.102	45.770	0.983	10.18	6.405	0.535	0.121	44.441	1.137	10.013	7.123	0.511
Standard error	0.012	2.482	0.112	0.541	0.989	0.060	0.004	0.628	0.067	0.263	0.960	0.053
t-value	8.479	18.444	8.765	18.82	6.477	8.917	30.728	70.761	17.060	38.058	7.423	9.596
Prob > t	0.003	0.000	0.003	0.000	0.007	0.003	0.000	0.000	0.000	0.000	0.005	0.002
Dependency	0.928		0.865		0.952		0.913		0.866		0.946	
Reduced Chi-Sqr	0.502		0.905		2.699		0.04339		0.22908		2.42109	
Residual sum of squares	1.506		2.715		8.098		0.13017		0.68725		7.26328	
R-square (COD)	0.995		0.992		0.975		0.9996		0.9979		0.9782	
Adj. R-Square	0.994		0.989		0.967		0.9995		0.9972		0.9709	
Number of points	5											
Degrees of freedom	3											

The assessments of n were arranged in three regions: first thing valuable for the range $2 < n < 10$, besides modestly hard range $1 < n < 2$, and in conclusion poor biosorption for $n < 1$ [31, 43, 61, 62]. However, the R^2 values for linear isotherm were found to 0.979 and 0.977 and for non-linear isotherm were 0.974 and 0.978 for Cd^{2+} onto AEA and AAO, respectively. The subsequent investigation demonstrated that the Freundlich model was not enough better fitted than Langmuir (by comparing R^2 values) to clarify the adsorption cycle.

The heat of the adsorption of the metal ion in the adsorbent layer decreases linearly because adsorbate-biosorbent interaction was taken into account by the Temkin isotherm [18]. The Temkin isotherm model was given in Eq. 11. The values of b_T and K_T were recorded by a linear plot of q_e versus $\ln C_e$ using slope and intercept. The regression coefficient (R^2) values of Cd^{2+} for AEA and AAO were recorded as 0.990 and 0.997 for linear isotherm and for non-linear isotherm 0.991 and 0.997 respectively (Table 2). The adsorption capacity A and intensity B have likewise been determined by Temkin plots (Fig. 3 c), which consider chemisorption of adsorbate onto the biosorbent [18, 48, 62]. The R^2 values for Langmuir isotherm were nearly equal to Temkin and more than the Freundlich model (Table 2). The analysis based on $Q_{\max}$ values showed the Langmuir model was best fitted for adsorption of Cd^{2+} onto AEA and AAO. The variance analysis and error functions between the experimental results and the empirical models are tabulated in Table 3.

3.2.7.1 Comparative study with other biosorbents The comparison of adsorption capacity ($Q_{\max}$) among AAO and AEA for Cd^{2+} ions with various biosorbents reported in the literature (Additional file 1, Table S1). The properties of each biosorbents such as adsorbent structure, functional groups, and surface area influenced the adsorption capacity in metal uptake [43]. As shown in Additional file 1, Table S1, AEA and AAO biomass have good adsorption capacity with 4.59 and 4.60 mg g^{-1} respectively for Cd^{2+} ions, compared with other biosorbents. Therefore, AEA and AAO biomass have important potential for the adsorptive removal of Cd^{2+} ions.

3.2.8 Biosorption kinetics

The pseudo-first-order and pseudo-second-order models were utilized to examine the kinetics of Cd^{2+} ion biosorption onto AEA and AAO. The system was recognized based on figuring the estimation of Q_{max} which was closer to the experimental value of Q_{max} with correlation coefficients (R^2). The relatively high value of R^2 demonstrated that the kinetics model effectively follows the Cd^{2+} adsorption kinetics.

3.2.8.1 Pseudo-first order kinetics The pseudo-first-order model of Lagergren, in light of the rate of adsorptive interaction [2, 33], showed in Fig. 4. It portrayed the rate of adsorption to be proportional to the number of occupied sites by metal ions [21, 44, 59–61]. Equation 12 demonstrated the model articulation in a direct structure and was used to determine the values of k_1 , $q_{e, \text{cal}}$ and R^2 (Table 3), and delineated in Fig. 4I.

The estimation of correlation coefficient (R^2) was ranged from 0.98 to 0.99 for AEA and 0.91 to 0.99 for the AAO biomass, which was almost closer to 1 at different concentrations, fitted in the first-order rate model. Additionally, the value of $q_{e, \text{cal}}$ was recorded from 4.16 to 15.27 for AEA and 6.27 to 47.28 for AAO, which had very large differences with the experimental data ($q_{t, \text{exp}}$) at different concentrations. This condition reveals that it couldn't be better fitted in the pseudo-first-order rate model.

3.2.8.2 Pseudo-second order kinetics Pseudo-second-order kinetic model expressed that the rate of adsorption is straightforwardly relative to the square of the quantity of empty dynamic locales. The overall rate of Cd^{2+} sorption was constrained by a chemical process [28, 49, 56, 59]. All the values of this model were determined by Eq. 13, represented in Fig. 4II, and shown in Table 4 at different concentrations for AEA and AAO. As appeared in Table 4, the correlation coefficients of pseudo-second-order kinetics were acquired in scope of 0.99 and 0.99 for AEA and AAO, individually, which were a lot more like 1.00 for the adsorption of Cd^{2+} ions.

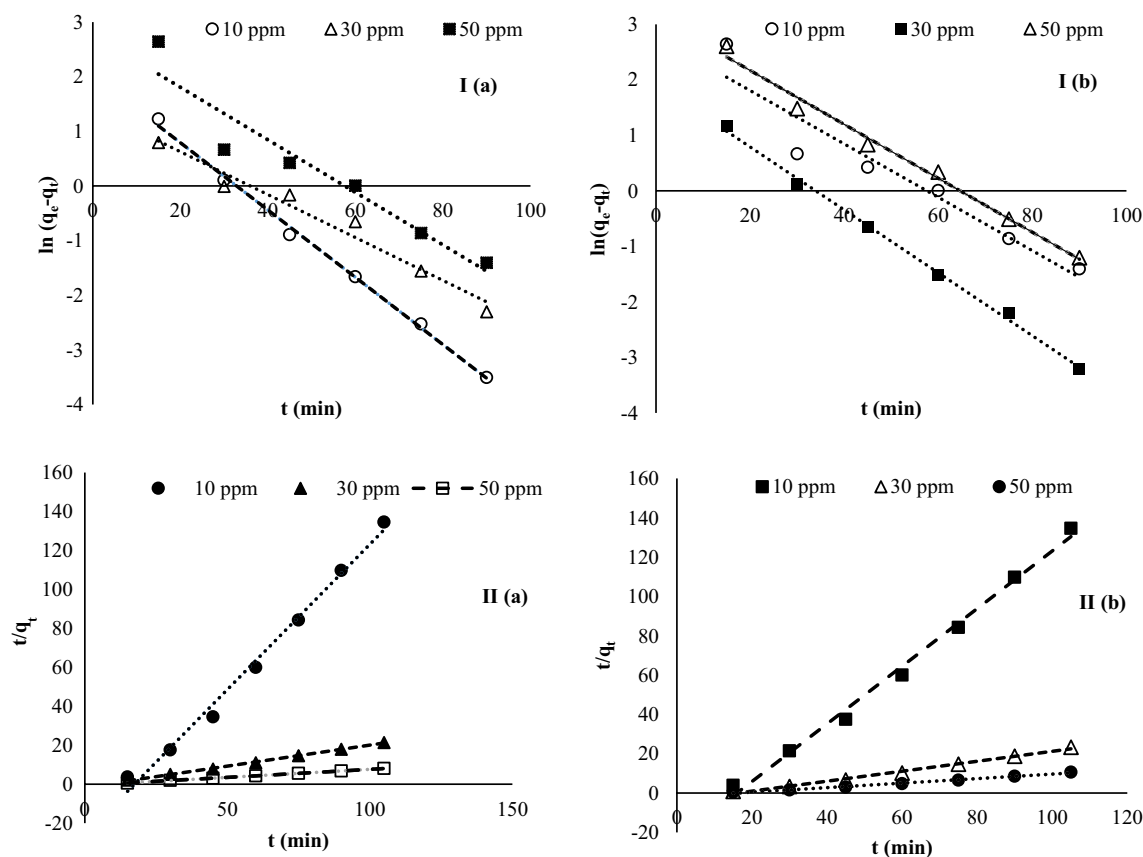


Fig. 4 Pseudo I first-order, II second-order sorption kinetics of Cd^{2+} ions onto activated **a** AEA, **b** AAO

Table 4 The comparative values of kinetics at different Cd^{2+} ion concentration data for activated AEA and AAO

Biosorbent	C_0 (mg L ⁻¹)	$q_{t, \text{exp}}$	Pseudo-first-order			Pseudo-second-order		
			$q_{e, \text{cal.}}$ (mg g ⁻¹)	k_1 (× 10 ⁻² min ⁻¹)	R^2	$q_{e, \text{cal.}}$ (mg g ⁻¹)	k_2 (× 10 ⁻² g mg ⁻¹ min ⁻¹)	R^2
AEA	10	0.59	6.25	5.56	0.991	0.670	8.600	0.990
	30	4.89	4.16	3.90	0.966	4.650	3.104	0.998
	50	12.99	15.27	4.81	0.988	12.120	0.720	0.999
AAO	10	0.78	6.27	5.92	0.910	0.682	9.160	0.990
	30	4.50	23.10	4.86	0.997	3.950	5.080	0.990
	50	9.70	47.28	4.77	0.989	8.720	0.725	0.990

Also, the estimations of $q_{e, \text{cal}}$ were recorded from 0.67 to 12.12 and 0.682 to 8.72, which was consistent with the experimental data ($q_{t, \text{exp}}$) for AEA and AAO respectively at different concentrations. It was revealed that the estimation of adsorption rate (k_2) decreased with the increase of Cd^{2+} ion concentrations, which might be a result of less rivalry for the adsorption dynamic locales at a lower concentration, the other way around.

Because of the over two reasons the process of adsorption best fitted with a pseudo-second-order kinetic model. Moreover, it may be finalized that, as the k_2 values for AEA and AAO were 8.6 and 9.16 g mg⁻¹ min⁻¹ for 10 mg L⁻¹; 3.104 and 5.08 g mg⁻¹ min⁻¹ for 30 mg L⁻¹ respectively, the adsorption capacity, in view on adsorption rate, the biomass follows the order AAO > AEA.

3.2.9 Desorption and regeneration experiments

The recycling of the biosorbent and recovery of heavy metals indicated that the Cd^{2+} desorption percentage increased to a decreased pH value of the solution, i.e. increases the concentration of HNO_3 . Desorption percent of the Cd^{2+} was almost reached 100% at pH 1.5 and it was minimum at pH 6 (Additional file 1, Fig. S5). The outcomes demonstrated that the cadmium was desorbed from AEA and AAO biosorbent completely and was prepared for reuse.

4 Conclusion

In this investigation, it was affirmed that AEA and AAO can be utilized as biosorbent for Cd^{2+} ion extraction from synthetic wastewater. It was concluded that the rate of adsorption was directly proportional to the biosorbent dose. Adsorption of Cd^{2+} ions on biomass decreases with the increase of the metal ion concentration and vice versa. The maximum adsorption was achieved at pH 7. The biosorption of Cd^{2+} ions was found spontaneous, endothermic, and irreversible onto AEA and AAO. The Langmuir adsorption isotherm along with Temkin isotherm was the best correlation coefficient for the biosorption of Cd^{2+} ions onto AEA and AAO. The AAO and AEA have almost the same adsorption capacity, Q_{max} and Langmuir isotherm models fitting well with linear and nonlinear isotherm models. The process of adsorption of Cd^{2+} ion onto AEA and AAO best fitted with a pseudo-second-order kinetic model. The biomass follows the order AAO > AEA at a given adsorption rate. Desorption percentage of the Cd^{2+} has nearly arrived at 100% at pH 1.5 and biomass adsorbent AEA and AAO can be reused for the expulsion of metal particles. The findings of the present exploration affirm that acid-activated AEA and AAO might be utilized to eliminate Cd^{2+} from aqueous solutions as ease and effective adsorbent.

Author contributions All authors have participated in: (a) conception and design, or analysis and interpretation of the data; and (b) drafting the article or revising it critically for important intellectual content. All authors read and approved the final manuscript.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary information file. Additional data and materials are available in the supplementary section.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication This is original work and has not published anywhere in any form. We do not have any objection for publication in your journal.

Competing interests Not applicable.

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References

1. Chowdhury S, Mazumder MJ, Al-Attas O, Husain T. Heavy metals in drinking water: occurrences, implications, and future needs in developing countries. *Sci Total Environ*. 2016;569:476–88. <https://doi.org/10.1016/j.scitotenv.2016.06.166>.
2. He T, Feng X, Guo Y, Qiu G, Li Z, Liang L, Lu J. The impact of eutrophication on the biogeochemical cycling of mercury species in a reservoir: a case study from Hongfeng Reservoir, Guizhou, China. *Environ Pollut*. 2008;154(1):56–67.
3. Tao HC, Zhang HR, Li JB, Ding WY. Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater. *Biores Technol*. 2015;192:611–7. <https://doi.org/10.1016/j.biortech.2015.06.006>.
4. Gupta VK, Rastogi A. Equilibrium and kinetic modeling of cadmium (II) biosorption by nonliving algal biomass *Oedogonium* sp. from an aqueous phase. *J Hazard Mater*. 2008;153(1–2):759–66. <https://doi.org/10.1016/j.jhazmat.2007.09.021>.
5. Lupea M, Bulgariu L, Macoveanu M. Biosorption of Cd (II) from aqueous solution on marine green algae biomass. *Environ Eng Manag J*. 2012. <https://doi.org/10.30638/eemj.2012.076>.
6. Yin J, Blanch HW. A bio-mimetic cadmium adsorbent: design, synthesis, and characterization. *Biotechnol Bioeng*. 1989;34(2):180–8. <https://doi.org/10.1002/bit.260340206>.
7. Jayakumar V, Govindaradjane S, Rajamohan N, Rajasimman M. Biosorption potential of brown algae, *Sargassum polycystum*, for the removal of toxic metals, cadmium and zinc. *Environ Sci Pollut Res*. 2021. <https://doi.org/10.1007/s11356-021-15185-7>.
8. Azouaou N, Sadaoui Z, Djaafri A, Mokaddem H. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: equilibrium, kinetics, and thermodynamics. *J Hazard Mater*. 2010;184(1–3):126–34. <https://doi.org/10.1016/j.jhazmat.2010.08.014>.
9. Babel S, Kurniawan TA. Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*. 2004;54(7):951–67. <https://doi.org/10.1016/j.chemosphere.2003.10.001>.
10. Leyva-Ramos R, Rangel-Mendez JR, Mendoza-Barron J, Fuentes-Rubio L, Guerrero-Coronado RM. Adsorption of cadmium (II) from aqueous solution onto activated carbon. *Water Sci Technol*. 1997;35(7):205–11. [https://doi.org/10.1016/S0273-1223\(97\)00132-7](https://doi.org/10.1016/S0273-1223(97)00132-7).
11. Gao M, Ma Q, Lin Q, Chang J, Ma H. A novel approach to extract SiO₂ from fly ash and its considerable adsorption properties. *Mater Des*. 2017;116:666–75. <https://doi.org/10.1016/j.matdes.2016.12.028>.
12. Abedi M, Salmani MH, Mozaffari SA. Adsorption of Cd ions from aqueous solutions by iron modified pomegranate peel carbons: kinetic and thermodynamic studies. *Int J Environ Sci Technol*. 2016;13(8):2045–56. <https://doi.org/10.1007/s13762-016-1002-7>.
13. Aksu Z. Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*. *Process Biochem*. 2002;38(1):89–99. [https://doi.org/10.1016/S0032-9592\(02\)00051-1](https://doi.org/10.1016/S0032-9592(02)00051-1).
14. Argun M, Dursun S, Ozdemir C, Karatas M. Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *J Hazard Mater*. 2007;141(1):77–85. <https://doi.org/10.1016/j.jhazmat.2006.06.095>.
15. Benaissa H, Elouchdi MA. Removal of copper ions from aqueous solutions by dried sunflower leaves. *Chem Eng Process*. 2007;46(7):614–22. <https://doi.org/10.1016/j.cep.2006.08.006>.
16. Chen H, Dai G, Zhao J, Zhong A, Wu J, Yan H. Removal of copper (II) ions by a biosorbent—*Cinnamomum camphora* leaves powder. *J Hazard Mater*. 2010;177(1–3):228–36. <https://doi.org/10.1016/j.jhazmat.2009.12.022>.
17. Chojnacka K, Chojnacki A, Gorecka H. Biosorption of Cr³⁺, Cd²⁺ and Cu²⁺ ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process. *Chemosphere*. 2005;59(1):75–84. <https://doi.org/10.1016/j.chemosphere.2004.10.005>.
18. de Heredia JB, Domínguez JR, Cano Y, Jiménez I. Nitrate removal from groundwater using Amberlite IRN-78: modelling the system. *Appl Surf Sci*. 2006;252(17):6031–5. <https://doi.org/10.1016/j.apsusc.2005.11.030>.
19. Deng S, Ting YP. Characterization of PEI-modified biomass and biosorption of Cu (II), Pb (II), and Ni (II). *Water Res*. 2005;39(10):2167–77. <https://doi.org/10.1016/j.watres.2005.03.033>.
20. Escudero LB, Maniero MÁ, Agostini E, Smichowski PN. Biological substrates: green alternatives in trace elemental pre concentration and speciation analysis. *Trends Anal Chem*. 2016;80:531–46. <https://doi.org/10.1016/j.trac.2016.04.002>.
21. Ho YS, Wase DJ, Forster CF. Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. *Environ Technol*. 1996;17(1):71–7. <https://doi.org/10.1080/09593331708616362>.

22. Iqbal M, Saeed A, Zafar SI. FTIR spectrophotometry, kinetics, and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste. *J Hazard Mater*. 2009;164(1):161–71. <https://doi.org/10.1016/j.jhazmat.2008.07.141>.
23. Jain SN, Gogate PR. Adsorptive removal of acid violet 17 dye from wastewater using biosorbent obtained from NaOH and H_2SO_4 activation of fallen leaves of *Ficus racemosa*. *J Mol Liq*. 2017;243:132–43. <https://doi.org/10.1016/j.molliq.2017.08.009>.
24. King P, Rakesh N, Lahari SB, Kumar YP, Prasad VSRK. Biosorption of zinc onto *Syzygium cumini* L.: equilibrium and kinetic studies. *Chem Eng J*. 2008;144(2):181–7. <https://doi.org/10.1016/j.cej.2008.01.019>.
25. Larous S, Meniai AH, Lehocine MB. Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination*. 2005;185(1–3):483–90. <https://doi.org/10.1016/j.desal.2005.03.090>.
26. Mirbagheri SA, Hosseini SN. Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. *Desalination*. 2005;171(1):85–93. <https://doi.org/10.1016/j.desal.2004.03.022>.
27. Murthy TK, Gowrishankar BS, Prabha MC, Kruthi M, Krishna RH. Studies on batch adsorptive removal of malachite green from synthetic wastewater using acid-treated coffee husk: equilibrium, kinetics and thermodynamic studies. *Microchem J*. 2019;146:192–201. <https://doi.org/10.1016/j.microc.2018.12.067>.
28. Özacar M, Şengil İA, Türkmenler H. Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin. *Chem Eng J*. 2008;143(1–3):32–42. <https://doi.org/10.1016/j.cej.2007.12.005>.
29. Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF. Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*. *Biores Technol*. 2006;97(18):2321–9. <https://doi.org/10.1016/j.biortech.2005.10.032>.
30. Pyrzynska K. Removal of cadmium from wastewaters with low-cost adsorbents. *J Environ Chem Eng*. 2019;7(1): 102795. <https://doi.org/10.1016/j.jece.2018.11.040>.
31. Sari A, Tuzen M, Citak D, Soylak M. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. *J Hazard Mater*. 2007;149(2):283–91. <https://doi.org/10.1016/j.jhazmat.2007.03.078>.
32. Sari A, Mendil D, Tuzen M, Soylak M. Biosorption of Cd (II) and Cr (III) from aqueous solution by moss (*Hylocomium splendens*) biomass: equilibrium, kinetic and thermodynamic studies. *Chem Eng J*. 2008;144(1):1–9. <https://doi.org/10.1016/j.cej.2007.12.020>.
33. Sari A, Tuzen M. Biosorption of Pb (II) and Cd (II) from aqueous solution using green alga (*Ulva lactuca*) biomass. *J Hazard Mater*. 2008;152(1):302–8. <https://doi.org/10.1016/j.jhazmat.2007.06.097>.
34. Sari A, Tuzen M. Biosorption of As (III) and As (V) from aqueous solution by macrofungus (*Inonotus hispidus*) biomass: equilibrium and kinetic studies. *J Hazard Mater*. 2009;164(2–3):1372–8. <https://doi.org/10.1016/j.jhazmat.2008.09.047>.
35. Sari A, Tuzen M. Kinetic and equilibrium studies of biosorption of Pb (II) and Cd (II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. *J Hazard Mater*. 2009;164(2–3):1004–11. <https://doi.org/10.1016/j.jhazmat.2008.09.002>.
36. Şentürk İ, Yıldız MR. Highly efficient removal from aqueous solution by adsorption of Maxilon Red GRL dye using activated pine sawdust. *Korean J Chem Eng*. 2020;37:985–99. <https://doi.org/10.1007/s11814-020-0526-1>.
37. Srivastava VC, Mall ID, Mishra IM. Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *J Hazard Mater*. 2006;134(1–3):257–67. <https://doi.org/10.1016/j.jhazmat.2005.11.052>.
38. Taşar Ş, Kaya F, Özer A. Biosorption of lead (II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies. *J Environ Chem Eng*. 2014;2(2):1018–26. <https://doi.org/10.1016/j.jece.2014.03.015>.
39. Tiwari P, Vishwakarma MC, Joshi SK, Kumar R, Bhandari NS. Equilibrium and thermodynamic studies of Pb (II), Cu (II), and Zn (II) adsorption onto *Dicliptera bupleuroides* leaves. *Chem Sci*. 2017;6(1):97–106.
40. Tong KS, Kassim MJ, Azraa A. Adsorption of copper ion from its aqueous solution by a novel biosorbent *Uncaria gambir*: equilibrium, kinetics, and thermodynamic studies. *Chem Eng J*. 2011;170(1):145–53. <https://doi.org/10.1016/j.cej.2011.03.044>.
41. Vieira AP, Santana SA, Bezerra CW, Silva HA, Chaves JA, de Melo JC, Airoidi C. Kinetics and thermodynamics of textile dye adsorption from aqueous solutions using babassu coconut mesocarp. *J Hazard Mater*. 2009;166(2–3):1272–8. <https://doi.org/10.1016/j.jhazmat.2008.12.043>.
42. Wang XS, Qin Y. Removal of Ni (II), Zn (II) and Cr (VI) from aqueous solution by *Alternanthera philoxeroides* biomass. *J Hazard Mater*. 2006;138(3):582–8. <https://doi.org/10.1016/j.jhazmat.2006.05.091>.
43. Wang F, Pan Y, Cai P, Guo T, Xiao H. Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. *Biores Technol*. 2017;241:482–90. <https://doi.org/10.1016/j.biortech.2017.05.162>.
44. Abd El-Latif MM, Elkady MF. Equilibrium isotherms for harmful ions sorption using nano zirconium vanadate ion exchanger. *Desalination*. 2010;255(1–3):21–43. <https://doi.org/10.1016/j.desal.2010.01.020>.
45. Feng Q, Wu D, Zhao Y, Wei A, Wei Q, Fong H. Electrospun AOPAN/RC blend nanofiber membrane for efficient removal of heavy metal ions from water. *J Hazard Mater*. 2018;344:819–28. <https://doi.org/10.1016/j.jhazmat.2017.11.035>.
46. Haider S, Ali FAA, Haider A, Al-Masry WA, Al-Zeghayer Y. Novel route for amine grafting to chitosan electrospun nanofibers membrane for the removal of copper and lead ions from aqueous medium. *Carbohydr Polym*. 2018;199:406–14. <https://doi.org/10.1016/j.carbpol.2018.07.026>.
47. Liu P, Borrell PF, Božič M, Kokol V, Oksman K, Mathew AP. Nanocelluloses and their phosphorylated derivatives for selective adsorption of Ag^+ , Cu^{2+} and Fe^{3+} from industrial effluents. *J Hazard Mater*. 2015;294:177–85. <https://doi.org/10.1016/j.jhazmat.2015.04.001>.
48. Lv Q, Hu X, Zhang X, Huang L, Liu Z, Sun G. Highly efficient removal of trace metal ions by using poly (acrylic acid) hydrogel adsorbent. *Mater Des*. 2019;181: 107934. <https://doi.org/10.1016/j.matdes.2019.107934>.
49. Yang P, Xu Y, Tuo J, Li A, Liu L, Shi H. Preparation of modified pomelo peel's pulp adsorbent and its adsorption to uranyl ions. *R Soc Open Sci*. 2019;6(3): 181986. <https://doi.org/10.1098/rsos.181986>.
50. Cruz CC, Da Costa ACA, Henriques CA, Luna AS. Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass. *Biores Technol*. 2004;91(3):249–57. [https://doi.org/10.1016/S0960-8524\(03\)00194-9](https://doi.org/10.1016/S0960-8524(03)00194-9).
51. Salazar-Rabago JJ, Leyva-Ramos R, Rivera-Utrilla J, Ocampo-Perez R, Cerino-Cordova FJ. Biosorption mechanism of Methylene Blue from aqueous solution onto White Pine (*Pinus durangensis*) sawdust: effect of operating conditions. *Sustain Environ Res*. 2017;27(1):32–40. <https://doi.org/10.1016/j.serj.2016.11.009>.

52. Tizo MS, Blanco LAV, Cagas ACQ, Cruz BRBD, Encoy JC, Gunting JV, Mabayo VIF. The efficiency of calcium carbonate from eggshells as an adsorbent for cadmium removal in aqueous solution. *Sustain Environ Res*. 2018;28(6):326–32. <https://doi.org/10.1016/j.serj.2018.09.002>.
53. Wang C, Hu X, Chen M, Wu Y. Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni, and Zn in sewage sludge from municipal and industrial wastewater treatment plants. *J Hazard Mater*. 2005;119(1–3):245–9. <https://doi.org/10.1016/j.jhazmat.2004.11.023>.
54. De Gisi S, Lofrano G, Grassi M, Notarnicola M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review. *Sustain Mater Technol*. 2016;9:10–40. <https://doi.org/10.1016/j.susmat.2016.06.002>.
55. Doğan M, Alkan M. Adsorption kinetics of methyl violet onto perlite. *Chemosphere*. 2003;50(4):517–28. [https://doi.org/10.1016/S0045-6535\(02\)00629-X](https://doi.org/10.1016/S0045-6535(02)00629-X).
56. Du T, Zhou LF, Zhang Q, Liu LY, Li G, Luo WB, Liu HK. Mesoporous structured aluminosilicate with excellent adsorption performances for water purification. *Sustain Mater Technol*. 2018;18: e00080. <https://doi.org/10.1016/j.susmat.2018.e00080>.
57. Guyo U, Matewere N, Matina K, Nharingo T, Moyo M. Fabrication of a sustainable maize stover-graft-methyl methacrylate biopolymer for remediation of methyl red contaminated wastewaters. *Sustain Mater Technol*. 2017;13:9–17. <https://doi.org/10.1016/j.susmat.2017.05.001>.
58. He HJ, Xiang ZH, Chen XJ, et al. Biosorption of Cd(II) from synthetic wastewater using dry biofilms from biotrickling filters. *Int J Environ Sci Technol*. 2018;15:1491–500. <https://doi.org/10.1007/s13762-017-1507-8>.
59. Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochem*. 1999;34(5):451–65. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5).
60. Ho YS. Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass by Cruz, CCV, da Costa, ACA, Henriques, CA, Luna, AS. *Biores Technol*. 2004;91(3):249–57. <https://doi.org/10.1016/j.biortech.2003.11.008>.
61. Ho YS, Ofomaja AE. Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *Biochem Eng J*. 2006;30(2):117–23. <https://doi.org/10.1016/j.bej.2006.02.012>.
62. Langmuir I. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J Am Chem Soc*. 1918;40(9):1361–403. <https://doi.org/10.1021/ja02242a004>.
63. Freundlich H. Über die adsorption in lösungen. *Zeitschrift für physikalische Chemie*. 1907;57(1):385–470.
64. Rafatullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater*. 2010;177(1–3):70–80. <https://doi.org/10.1016/j.jhazmat.2009.12.047>.

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