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Research Article

Efficient Sequestration of Cr(VI) from Aqueous Solution Using Biosorbent Derived from *Arundo donax* Stem

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The potential of a biosorbent derived from *Arundo donax* stem, a readily available agricultural product, was examined to remove Cr(VI) from water. Various techniques such as XRD, FTIR, SEM, and EDX were used for the characterization of the prepared adsorbent. The optimal pH for Cr(VI) biosorption was found to be 2.0. The experimental data best suits the Langmuir isotherm model and pseudosecond-order kinetics. The maximum biosorption capacity (q_{max}) of the investigated biosorbent for Cr(VI) was evaluated to be 76.92 mg/g by the Langmuir model. From the results of the Cr(VI) biosorption using charred *Arundo donax* stem powder (CADSP), it can be a novel, cost-efficient, and effective material for removing Cr(VI) from water and wastewater.

1. Introduction

Humans and other living species require water to survive. Various water sources, including springs, streams, canals, reservoirs, wells, and rivers, are polluted because of human activity. Major contaminants of water include suspended matter, waste and chemical contamination, direct discharge of effluents, and oxygen depletion. Heavy metals and metalloids are among the most common chemical contaminants, and because of their toxicity and carcinogenicity, they constitute a significant source of water contamination [1].

Because heavy metals can be found in significant concentrations in industrial wastewater, it is cleaned before being disposed of to prevent water pollution. Heavy metals are present in high proportion in the wastewater released into the receiving water body, which will have major negative effects on the ecosystem and cause a variety of diseases and problems [2]. Industrial growth, urbanization, and anthropogenic pollution are examples of human activities that contribute to heavy metals occurrence and accumulation in the surroundings. Heavy metal ions such as Cu(II), Cr(VI)/Cr(III), Cd(II), As(III)/As(V), Pb(II), Hg(II), Ni(II), and Zn(II) are commonly detected in contaminated water [3].

Chromium is a highly harmful heavy metal that can be found in a variety of industrial and polluted effluents. Lung cancer, ulcers, nasal septum perforation, nervous system, and renal damage are all caused by chromium (VI) [4]. Cr(VI) compounds can cause skin disorders when they come into contact with the skin. Because of its oxidizing capacity and the creation of free-radicals during the conversion of Cr(VI) to Cr(III) [5]. Numerous industrial processes, such as metal polishing, iron and steel production, and chemical manufacture, emit heavy metals into the atmosphere [6]. In nature, mainly Cr(III) and Chromium (VI) are persistent enough to be detected; however, they can be found in a range of oxidation states. The hexavalent type is more harmful than the trivalent one, which is linked to cancer and mutation [7]. Cr(VI) is commonly excreted as oxyanions like chromate and dichromate ions in wastewater, and the latter is the most harmful. Due to its acute lethal effects on human health, the WHO set a maximum exposure limit for Cr(VI) in drinkable water of 0.05 mg/L [8].

A variety of physicochemical techniques have been established for removing toxic metals or non-metals from water. Precipitation, ion exchange, electrochemical deposition, resin chelation, solid-phase extraction, reverse osmosis, and coagulation are some of the methods used [9]. These procedures, however, have drawbacks, including insufficient removal of metals; large reagents and energy demands; and the production of toxic waste [10].

Biosorption is a cutting-edge method that is both effective and cost-effective. As a result, metals that were before impossible to remove have become simple and efficient to remove. Biosorption has several important advantages over other traditional treatment methods, including minimal price, high performance, reduction of chemical and biological waste, rejuvenation of biosorbent through desorption operations, and the potential for recovery of metals [11]. Certain agricultural raw waste products have gained popularity in recent years such as cocoa shell [12], potato peel [13], rice husk [14], olive stone [15], garlic peel [16], sawdust [17], banana peel [18], *Carica papaya* seed [19], *Anabaena* and *Vetiveria* [20], coconut husk [21], sweet lime peels [22], date tree leaves [23], and sugarcane bagasse [24] were studied for their efficiency in eliminating metals from effluents.

Arundo donax, which is frequently found as bio-waste and has several functional groups on its surface and does not release soluble contaminants in treated water, makes it the ideal option for this study. *Arundo donax* stem powder offers unique morphological and physiological features, as well as tolerance to high amounts of heavy metals and unfavorable environments when used as a bioadsorbent. Its principal components are pectin, lignin, hemicellulose, and cellulose, and it has structural features that can be used to bind metals. It's a substance with a lot of promise that's commonly employed in environmental protection [25]. According to the best of our knowledge, there has been no study that has been reported in the literature of CADSP that investigates the adsorptive removal of Cr (VI). As a result, CADSP has been suggested for use as an innovative adsorbent in the process of removing Cr (VI) from the aqueous solution. The crucial objective of this research was to look at the biosorption capacity of CADSP for Cr (VI) ions from water. FTIR, XRD, SEM, and EDS characterization techniques were used to characterize adsorbents. The biosorption effectiveness was also studied for contact time, pH, and initial Cr (VI) concentration.

2. Materials and Methods

2.1. Reagents. Reagents of analytical grade were utilized, and they were not purified further. In a 0.1 N HNO_3 solution, a 1000 mg/L potassium dichromate stock solution was prepared. Dilutions were made in 0.1 N nitric acid to make working solutions. The UV-vis spectrophotometer was used to determine the initial and equilibrium concentrations of Cr(VI) in the solution.

2.2. Preparation of Adsorbent from Arundo donax Stem. *Arundo donax* stems were collected from several areas throughout Kirtipur, Kathmandu, Nepal. They were cleaned with water and then exposed to the sun for five days to dry entirely. Using a mechanical grinder, the dried *Arundo donax* stems were broken into small pieces and powdered. After that, the powder was sieved at 212 μm to obtain a precise particle size. This *Arundo donax* stem powder was regarded as raw *Arundo donax* stem powder (RADSP).

At room temperature, RADSP was treated with concentrated sulphuric acid. A high cellulose concentration in the RADSP is possible, and acid modification may well be able to produce an environment that is favorable to opening the ring. In addition to this, it produces a significant extent of microporosity and expands the surface area of the material [26]. A complete reaction was ensured by mixing concentrated H_2SO_4 in a 1 : 3 (W/V) ratio with RADSP and letting the mixture sit for 24 hrs. Washing with distilled water till the pH was neutrally eliminated the extra acid. After drying for 6 hours at 80°C in a hot air oven, it was sieved to a 212 μm particle size. The charred *Arundo donax* stem (CADSP) adsorbent was finely pulverized and sealed in an airtight container.

2.3. Characterization Techniques. The surface functional group of the sample was characterized using FTIR spectroscopy on an IR AFFINITY-1Shimadzu (Shimadzu, Kyoto, Japan) spectrometer. SEM images of CADSP and Cr (VI) adsorbed CADSP were taken on the JEOL-JSM-6700F instrument (Jeol Ltd., Tokyo, Japan) to identify the morphology and elemental composition. The crystallinity of the biosorbent was determined by X-ray diffraction analysis using an X-ray diffractometer (Rigaku Co., Japan).

2.4. Batch Biosorption and Kinetics Study. In a 25 mL reagent container, 25 mg of raw and charred *A. donax* stem powder was treated with 25 mL of Cr(VI) with a known starting concentration. At room temperature, the mixture was stirred for 24 hours on a mechanical shaker. The filtrates from the solution's filtering were used to measure the residual metal ion concentration. To acquire equilibrium data, batch biosorption tests were conducted at room temperature with various pH, initial Cr(VI) concentrations, and contact times (10 minutes to 360 minutes). All the trials were done in triplicate and the average was calculated.

The following equations were used to determine the capacity of biosorption at equilibrium q_e (mg/g) and biosorption efficiency.

$$q_e\,(\text{mg/g}) = \frac{C_0 - C_e}{M} \times V, \tag{1}$$

$$\text{Biosorption efficiency}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100, \tag{2}$$

where C_0 represents the starting concentration (mg/L), C_e represents the Cr(VI) equilibrium time concentrations (mg/L), M represents the biosorbent mass (g), and V represents the volume of water in litre [16, 27].

2.4.1. Isotherm Study. Monolayer biosorption on a biosorbent's surface is represented using the Langmuir

isotherm model. As seen below, it is expressed both non-linearly and linearly by the following equations, respectively [28].

$$q_e = \frac{qm \cdot b \cdot Ce}{1 + b \cdot Ce}, \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{qm\,b} + \frac{Ce}{qm}, \tag{4}$$

where, the Langmuir constant is b (L/mg), while the maximum adsorption capacity is q_m (mg/g).

The Freundlich isotherm, which is articulated utilizing nonlinear equations, determines multilayer biosorption on a heterogeneous surface [29],

$$q_e = K_F\left(C_e\right)^{(1/n)}, \tag{5}$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e. \tag{6}$$

Biosorption capacity is represented by the Freundlich constant K_F ((mg/g) (L/mg)$^{1/n}$), while biosorption intensity is represented by the Freundlich exponent n.

2.4.2. Biosorption Kinetics. The biosorption kinetics were determined by pseudo-1st-order and pseudo-2nd-order models, that revealed the regulating mechanism of Cr(VI) biosorption on the biosorbent. Equation (7) expresses the pseudofirst order linear equation as [30],

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t. \tag{7}$$

k_1 (mg/g·min) is the pseudo first order rate constant, and q_t (mg/g) is the sorption capacity at time t (mg/g). Equation (8) represents the pseudo-2$^{\text{nd}}$-order linear equation as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t, \tag{8}$$

where k_2 (g/mg·min) represents the rate constant of the pseudo-2nd-order model [27].

2.4.3. Thermodynamic Studies. The calculation of the change in thermodynamic parameters namely Gibbs free energy (ΔG^{o}), entropy (ΔS^{o}), as well as enthalpy (ΔH^{o}) was done using experimental data and isotherm constants at the temperatures of 298 K, 308 K, and 318 K. The ΔG^0 values were calculated employing the following equation:

$$\triangle G^0 = -RT\ln K_C, \tag{9}$$

where R is the universal gas constant with the value of 8.314 J·mol^{-1}·K^{-1}, T is the temperature in Kelvin and K_C is the dimensionless thermodynamic equilibrium constant. The Langmuir constant (b) calculated from the experiment was employed to determine the value of K_C. When a biosorption experiment is conducted in water and b has units of L/g, the K_C may easily be obtained as a dimensionless parameter by applying the following equation [31–33]:

$$K_C = b \times 55.5 \times 1000 \times \mathrm{M}_W, \tag{10}$$

where M_w denotes the molar mass of chromium (51.99 g·mol^{-1}), and the factor 55.5 represents the number of moles of pure water in one litre of solution (~1,000 g/L divided by 18 g/L).

Also, ΔG^0 is associated with ΔH^0 and ΔS^0 at a given temperature using the given equation:

$$\triangle G^{\circ} = \triangle H^{\circ} - \mathrm{T}\triangle S^{\circ}. \tag{11}$$

From equations (9) and (11), the Van't Hoff equation is obtained [34].

$$\ln K_C = -\frac{\triangle H^{\circ}}{RT} + \frac{\triangle S^{\circ}}{R}. \tag{12}$$

2.4.4. Desorption Studies. The biosorption-desorption cycle was used to test the efficacy of adsorbents that would be employed for biosorption several times. 50 mL of a known concentration and pH-optimized metal ion solution was treated with 50 mg CADSP in reagent bottles and shaken for 24 hours. The equilibrium concentration was then obtained to compute the amount of adsorbed. The residue was then combined with 50 mL of 1 N NaOH solution in the same reagent bottle, agitated for 24 hours before being filtered, and the residue was kept aside for further desorption. Equation (13) expresses the percent desorption (% D) of Cr(VI).

$$\%D = \frac{A_d}{A_a} \times 100, \tag{13}$$

where A_a denotes the amount of Cr(VI) ions adsorbed in mg/g and A_d denotes the desorbed amount in mg/g [35, 36].

3. Results and Discussion

3.1. Adsorbent characterization. In Figure 1 demonstrates the mass titration results obtained with three different NaCl concentrations, and the point of zero charges (pH_{PZC}) of CADSP was determined to be 4.0. When the pH of the solution is less than pH_{PZC}, the electrostatic interaction between the anions and the positively charged surface of the biosorbent causes the surface to become positively charged, promoting the biosorption of anionic substances, whereas when the solution's pH is higher than pH_{PZC}, cationic substances biosorption is advantageous. The results show that the biosorption of Cr(VI) anionic species is more suitable at pH lower than pH_{PZC} 4.0. Titrations with three different concentrations of NaCl, namely 0.01 M, 0.05 M, and 0.1 M with CADSP adsorbent, suggest that anionic Cr(VI) biosorption is more favorable at pH lower than pH_{PZC} 4.0.

A broad band at 3398.57 cm^{-1} in the FTIR spectra of RADSP shows the presence of (-OH) groups in biomass. This peak shift becomes stronger in the case of CADSP owing to the ring-opening and the considerable amount of -OH present (Figure 2). The vibration of C-H stretching is responsible for the peak at 2954.94 cm^{-1} in RADSP. In

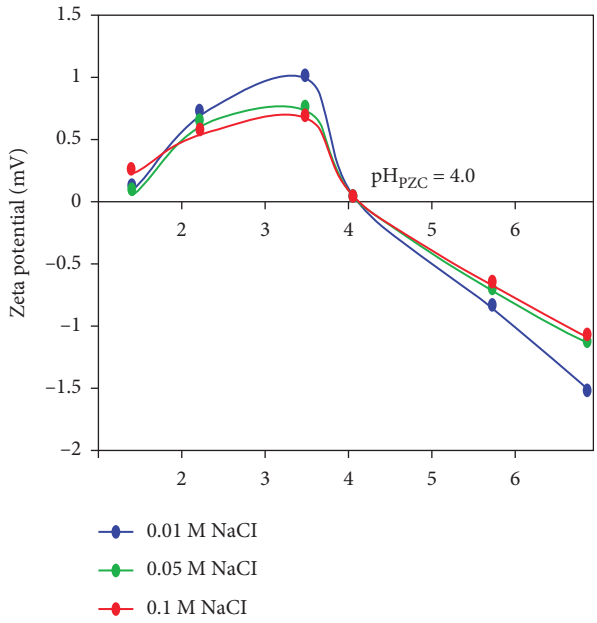


Figure 1: Determination of point zero charge using 0.01 M, 0.05 M, and 0.1 M NaCl.

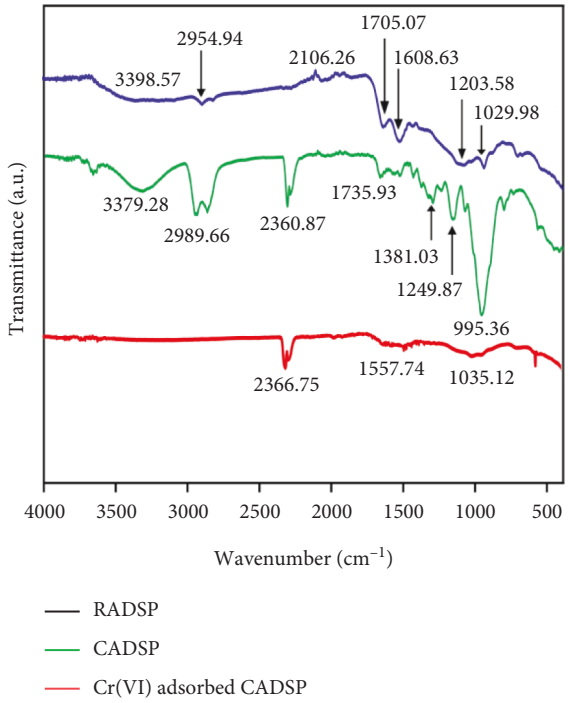


Figure 2: FTIR spectrum of RADSP and CADSP.

RADSP, a peak at 1705.07 cm^{-1} is allocated to the carbonyl group's carbonyl stretching vibration [35, 37]. The spectra of the CADSP revealed a change in the intensity and frequency range of -OH and C=O stretching. In the case of CADSP compared to RADSP, there is also the formation of new peaks and the disappearance of a few peaks. In Cr(VI) adsorbed CADSP, the -OH peak has completely vanished in contrast to CADSP, this is most likely because -OH groups have a role in the biosorption of Cr(VI). Furthermore, the

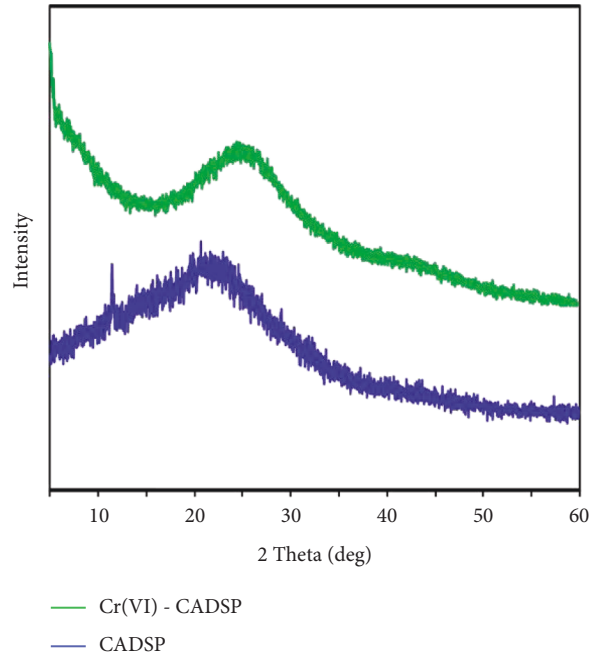
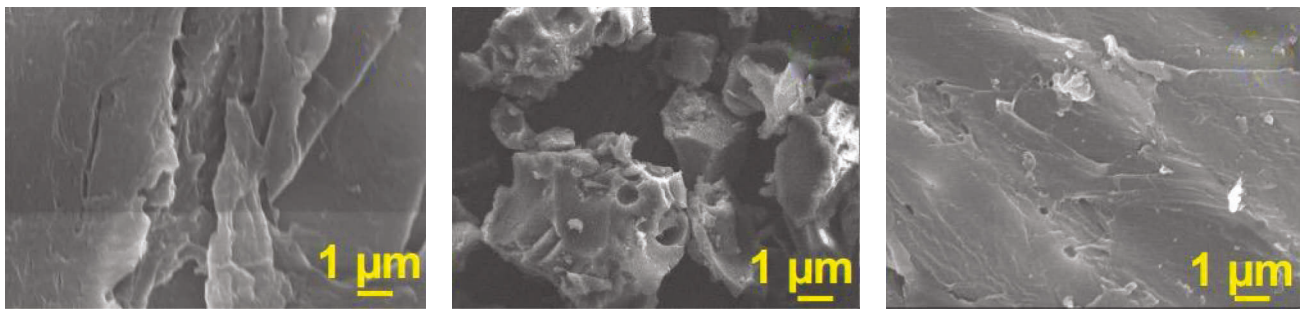


Figure 3: XRD of CADSP and Cr(VI) adsorbed CADSP.

steep peaks that existed in CALS have vanished, and a switch in the intensity of existing peaks revealed the involvement of chemical reactions, which result in the breakdown of chemical bonds. All the foregoing characteristics point to a successful chemical conversion of RADSP to CADSP, with high chromium biosorption on the CADSP.

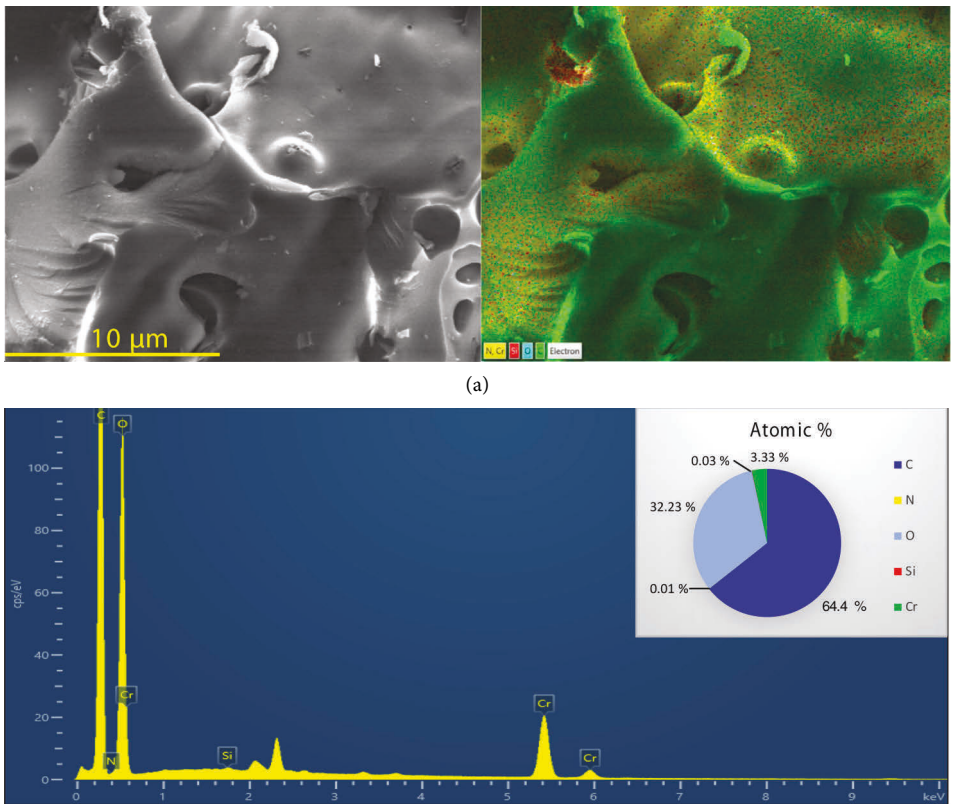
The XRD pattern was used to determine if the adsorbent was crystalline or amorphous and Figure 3 depicts the XRD pattern of CADSP and Cr(VI) adsorbed CADSP. The week and dispersed peaks at 2θ are equal to 22° in CADSP, which is the distinctive peak of cellulose due to the presence of an amorphous structure, which suggests CADSP is made from cellulose with amorphous areas [38]. Furthermore, little shift in the peak position in Cr(VI) adsorbed CADSP without any sharp peaks suggests that the adsorbent was amorphous in nature throughout the process.

The surface properties of RADSP, CADSP, and Cr(VI) adsorbed CADSP were investigated using SEM. Compared to RADSP (Figure 4(a)), the surface of CADSP was found to be more porous (Figure 4(b)) with various shapes, sizes, and irregular rough surfaces indicating that the hydrolysis process occurred on the surface of RADSP due to the reaction of conc. H_2SO_4. The rough shapes developed by the H_2SO_4 having pores and cavities might be because of the breakage of the polymeric network of raw *Arundo donax* and its transformation to microscopic, high-surface-area particles. The chromium Cr(VI) ion biosorption reduced the roughness of the surface in Cr-CADSP having more shining particles (Figure 4(c)) [39]. EDX confirm the biosorption of Cr(VI) at 0.57 keV, 5.36 keV, and 5.82 keV (Figure 5). The primary components of *A. donax* are cellulose, hemicelluloses, and lignin, which are represented by C, O, and Si, respectively, with 64.4, 33.23, and 0.03 wt percent. The amount of Cr adsorbed in CADSP was found to be 3.33 wt%



(a) (b) (c)

Figure 4: SEM image of (a) RADSP, (b) CADSP, and (c) Cr(VI)-CADS.



(a)

(b)

Figure 5: (a) EDX electron and layered images and (b) EDS atomic percentage of the Cr(VI)-loaded CADSP.

which revealed that a large amount of Cr(VI) had been deposited onto the *A. donax* biomass throughout the biosorption process.

3.2. Effect of the pH. The chemical properties of metal ions, as well as the ionic states of binding sites contained in the adsorbent examined in aqueous solutions, are all substantially influenced by the pH value [40]. Figure 6 displays that pH 2 is ideal for the maximal biosorption and that as pH rises, Cr(VI) biosorption declines. The percentage removal was dramatically raised from 27.56 percent for RADSP to 90.01 percent for CADSP at optimum pH, demonstrating the major difference between the two adsorbents. Cr(VI) exists in several oxyanion forms, including $Cr_2O_7^{2-}$, $HCr_2O_7^{-}$, CrO_4^{2-}, and $HCrO_4^{-}$ [35, 41, 42].

CrO_4^{2-} ions are the predominant type of ions in a basic media with a pH greater than 6. The ions $HCrO_4^{-}$ and $Cr_2O_7^{2-}$ are in equilibrium in an acidic solution with a pH of 1 to 6, but $HCrO_4^{-}$ is the main species [43, 44].

Because the predominant form of Cr(VI) at pH 2 is $HCrO_4^{-}$, and the solution includes a considerable number of H^+ ions at this pH, exterior protonation of biosorbent results in the creation of a positively charged adsorbent. These protonated interfaces of sorbents react with Cr(VI) anion by an electrostatic attraction phenomenon due to which biosorption is in favor i.e, $HCrO_4^{-}$ being adsorbed onto biosorbent surface [45]. At pH 1, despite the existence of an

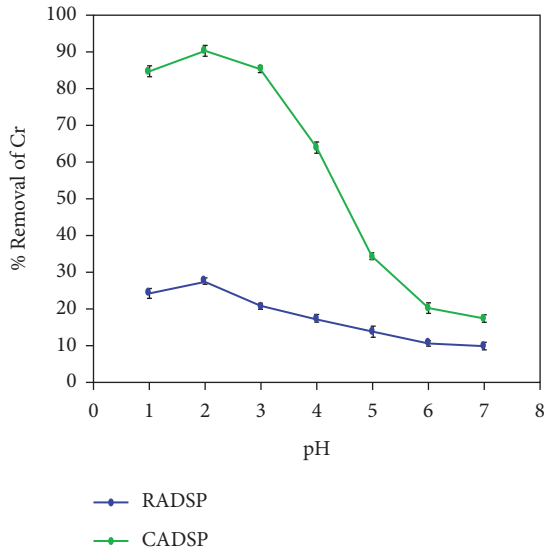


Figure 6: Influence of pH on Cr(VI) biosorption onto RADSP & CADSP.

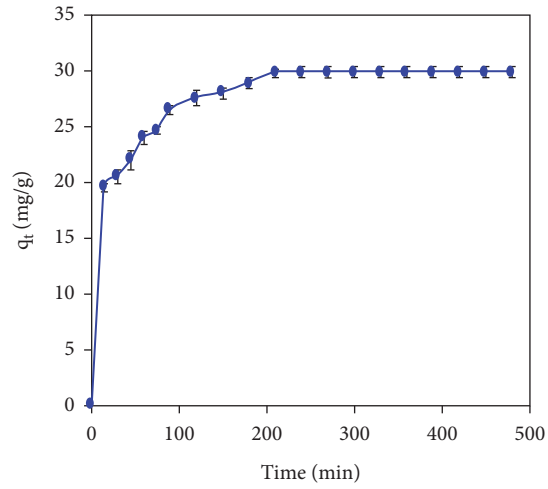


Figure 7: The influence of the agitation time for Cr(VI) biosorption on CADSP.

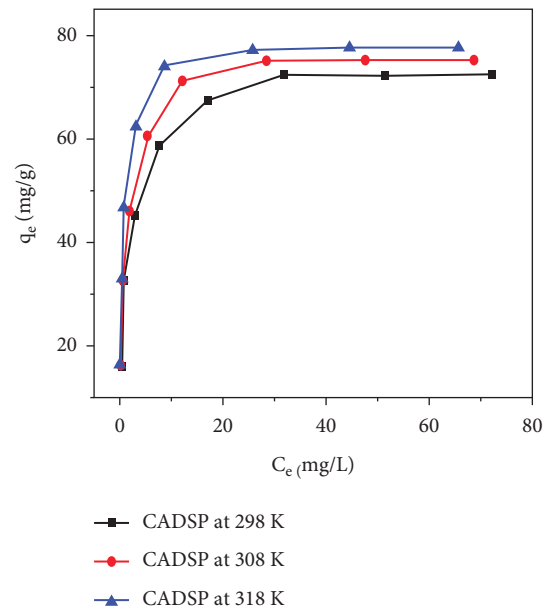


Figure 8: Biosorption isotherm for Cr (VI) onto CADSP at different temperatures (298-318 K).

acidic medium, there are still additionally available protons that can help to reduce C(VI) to Cr (III). Because of competitiveness among protons, Cr(III) species, and active sites on the biosorbent's surface, metal cations react with positively charged biosorbent's surface via electrostatic repulsion, so biosorption is less favorable than that of pH 2. When pH rises, the protonation of the adsorbent surface decreases, resulting in a decrease in percent biosorption. Dissociation of the acidic functional group also increased the complexation between Cr(III) (obtained from Cr(VI) reduction) and an anionic functional group, lowering the specific biosorption of Cr(VI) [46]. Because raw RADSP showed a low potentiality compared to CADSP, further study was primarily focused on CADSP.

3.3. The Influence of Contact Time for Biosorption of Cr(VI). By changing the contact time while maintaining the other variables constant, the contact time effect for chromium biosorption on CADSP was examined (Figure 7). The presence of significant biosorption sites causes the adsorption rate of Cr(VI) to increase at initially [45, 47]. As time passed, Cr(VI) ion gradually occupied the biosorption sites, and the rate of Cr(VI) biosorption gradually increased until 210 minutes. After that, there is no significant rise in Cr(VI) biosorption rate, and it reaches equilibrium after 240 minutes.

3.4. Batch Biosorption Isotherm Studies. The adsorption 'isotherm's fluctuation in initial Cr(VI) concentration was assessed for its adsorption capacity. Figure 8 shows the Cr (VI) adsorption isotherms onto CADSP at various temperatures between 298 and 318 K. The findings show that the adsorption capacity increased fast when the arsenate ion concentration rose from low to high, then rose gradually until reaching saturation (plateau) at high concentrations. The high adsorption rate in the early stage may be explained by the growing availability of vacant sorption sites of biosorbent. There are no longer any locations accessible for further adsorption since the adsorption capacity has achieved a plateau at a high concentration region. Additionally, at the examined range of temperatures, the adsorption capacity of CADSP rises with temperature, indicating an endothermic process of adsorption.

The best-fit isotherm model for Cr(VI) biosorption onto CADSP was determined by analyzing the experimental data using the well-known Langmuir and Freundlich isotherm equations. Table 1 lists the calculated values for the Langmuir and Freundlich parameters along with the corresponding R^2 values. It was observed that the correlation coefficient (R^2) values for the Langmuir isotherm were found to be greater than that of Freundlich isotherm. As a result,

Table 1: Isotherm parameter determined for Cr(VI) biosorption onto CADSP at pH 2.

Isotherm model	Parameter	298 K	308 K	318 K
Langmuir	q_m (mg/g)	74.24	77.63	81.493
	b (L/mg)	0.650	0.942	1.531
	R^2	0.999	0.999	0.999
Freundlich	K_F (mg/g)·(L/mg)$^{1/n}$	28.75	32.05	36.89
	n	3.84	3.97	4.38
	R^2	0.834	0.814	0.801

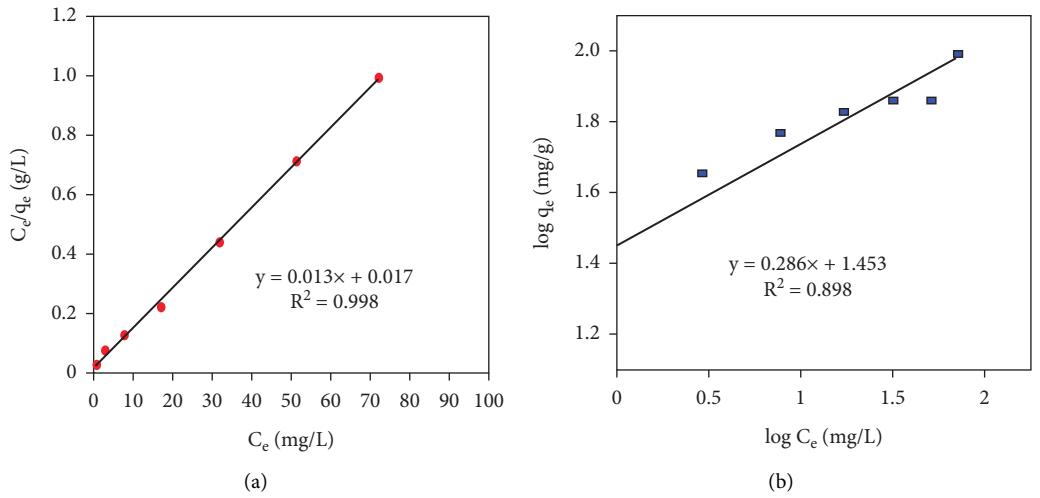


Figure 9: (a) Langmuir, and (b) Freundlich plots for Cr(VI) biosorption using CADSP at 298 K.

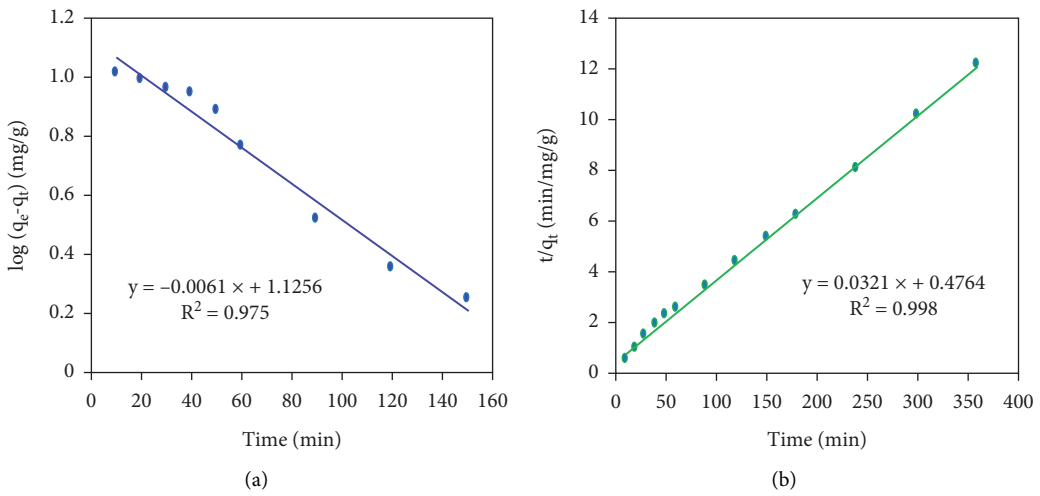


Figure 10: (a) Pseudo-1st-order, and (b) pseudo-second-order kinetic plots for the biosorption of Cr(VI) onto CADSP.

we may conclude that the biosorption isotherms most closely match the linear Langmuir isotherm model. It signifies a monolayer biosorption and a uniform distribution of reactive sites on the surface of the biosorbent [48]. The linearized Langmuir and Freundlich isotherm plots at room temperature of 298 K are shown in Figure 9.

3.5. Batch Kinetic Studies. The kinetics of Cr(VI) biosorption on CADSP at optimal pH 2 was investigated using pseudo-1st-order and pseudo-2nd-order models (Figure 10). The plot analysis revealed that the pseudo-2nd-order model had a higher R^2 than the pseudo-1st-order. Additionally, the biosorption of Cr(VI) onto CADSP followed pseudo-2nd-order kinetics, as evidenced by the close match between experimental and theoretical findings of q_e (Table 2) [45, 49].

The q_{max} of Cr(VI) utilizing CADSP is compared to the q_{max} of many other adsorbents that have been found in the literature (Table 3). The Cr(VI) biosorption capability of CADSP is superior among the described adsorbents,

Table 2: Kinetic parameters determined for the Cr(VI) biosorption onto CADSP.

Adsorbent	q_{exp} (mg/g)	Pseudo-first order			Pseudo-second order		
		K_1 (min^{-1})	q_e (mg/gm)	R^2	K_2 (mg/g/min)	q_e (mg/gm)	R^2
CADSP	29.752	0.015	14.521	0.975	0.0022	31.250	0.998

Table 3: Comparing the biosorption capacities of several biosorbents for Cr(VI) with CADSP.

S.N.	Biosorbent	pH	q_m (mg/g)	Reference
1	*Arthrobacter viscosus* biomass	2.0	20.37	[50]
2	Waste newspaper	3.0	59.88	[51]
3	Coconut husk	2.0	29.0	[21]
4	Cactus fruit	2.0	18.5	[52]
5	Carbon slurry	2.0	15.24	[53]
6	Giant reed	3.0	18.80	[54]
7	Nutshell powder	2.0	72.12	[55]
8	Coconut coir pith	2.0	76.3	[56]
9	Human hair	1	9.85	[57]
10	Fish scale	5	18.34	[58]
11	Charred betel nut waste	2	1.51 mmol/g	[59]
12	*Modified Arundo donax* stem	2.0	76.92	Present study

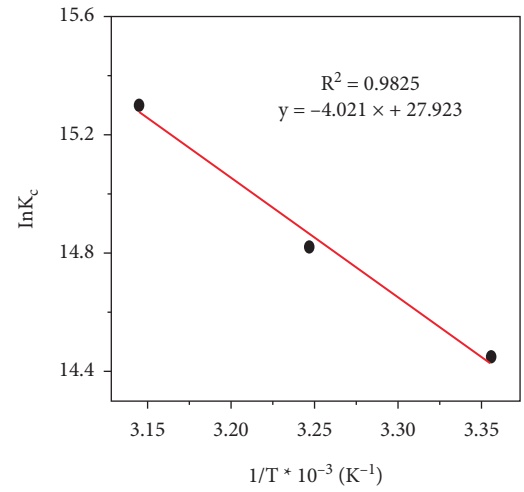


Figure 11: Van't Hoff plot of lnKC as a function of 1/T.

implying that CADSP might be a viable choice for removing Cr(VI) from water samples.

3.6. Comparison of Cr (VI) Biosorption Capacities of Various Adsorbents with CADSP. As shown in Table 3, the maximum bisorption capacity (q_m) of CADSP for Cr (VI) estimated using the Langmuir model at room temperature (298 K) was 76.92 mg/g. This value is higher than that of many materials reported in prior studies. It implies that CADSP may work well and hold promise as a biosorbent for the removal of Cr (VI) from polluted water.

3.7. Thermodynamic Studies. The thermodynamic parameters were assessed from the biosorption isotherm investigations of Cr (VI) on CADSP at temperatures 298-318 K. The values of ΔH^0 and ΔS^0 were derived from the van't Hoff plot of ln K_C vs. 1/T as displayed in Figure 11, whereas the value of ΔG° was determined directly from Equation (9). A straight line with $R^2 = 0.982$ results from the plot. The values of the assessed thermodynamic parameters are shown in Table 4. All the examined temperatures (298-318 K) had negative ΔG° values, indicating that this adsorption process was possible, thermodynamically advantageous, and spontaneous [34, 41]. A process of endothermic sorption is suggested by the positive value of ΔH°. The increased randomness of Cr (VI) ions on the surface of CADSP is also shown by the positive value of ΔS^0.

3.8. Desorption Analysis of CADSP. NaOH solution of different concentrations was used as an eluent for the desorption study. Figure 12(a) shows the effect of eluent concentration on CADSP. As pH study revealed that the

Table 4: Thermodynamic parameters of CADSP and Cr(VI) system.

T (K)	b (L/mol)	ΔG^0 (kJ/mol)	ΔH^0 (J/mol)	ΔS^0 (J/mol/K)
298	0.6507	−35.80		
308	0.9422	−37.95	33.43	232.16
318	1.5312	−40.45		

biosorption is effective at lower pH, it indicated that an alkaline solution could be an effective eluent. As a result, NaOH solution can be used to desorb Cr(VI) from exhausted biosorbent. The experiment showed that the desorption percentage enhanced from 18.45% to 100% with the increase of NaOH concentration from 0.05 to 1.00 M. When the concentration of the NaOH solution is increased to a high level, there is a possibility that the adsorbed Cr(VI) ions will be replaced by the hydroxyl ions. In addition, a larger concentration of NaOH may have also played a part in the destruction of the CADSP's chemical integrity. To reduce the cost, the reusability of the adsorbent is significant. Because $HCrO_4^-$ is the main form of Cr(VI) at optimal pH 2, a considerable quantity of H^+ ions may be exposed in the solution. Because of the protonation of the surface, the adsorbent develops a positively charged surface. Because of the electrostatic attraction between the protonated surfaces of adsorbents and $HCrO_4^-$, it adsorbs onto the surface of CADSP [45].

The regeneration studies of the prepared CADSP were assessed by subjecting four series of adsorption/desorption cycles (Figure 12(b)). Cr(VI) sorption capacity of CADSP was decreased by only 15.15% after four cycles, suggesting that the CADSP can be reused. Hence, the adsorbent showed the potential to be reused for another cycle without

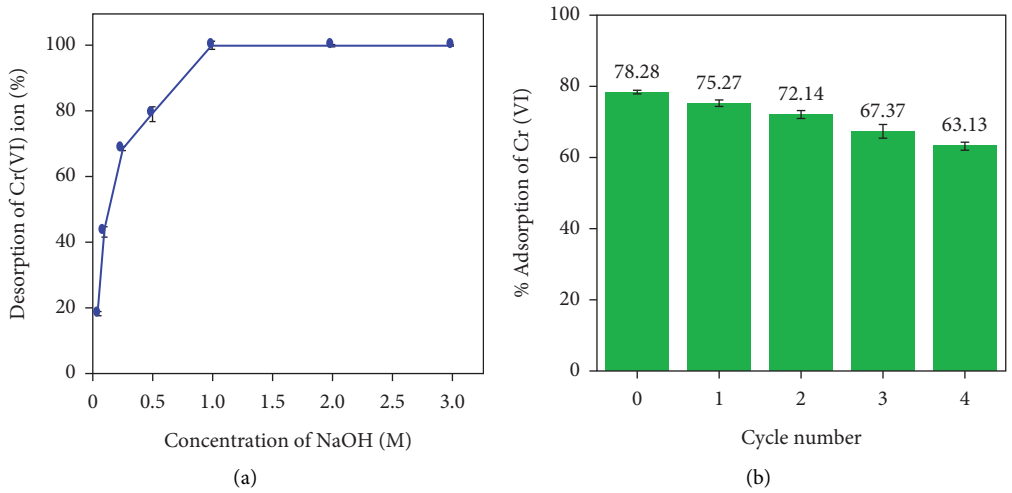
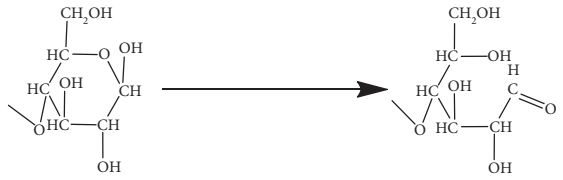
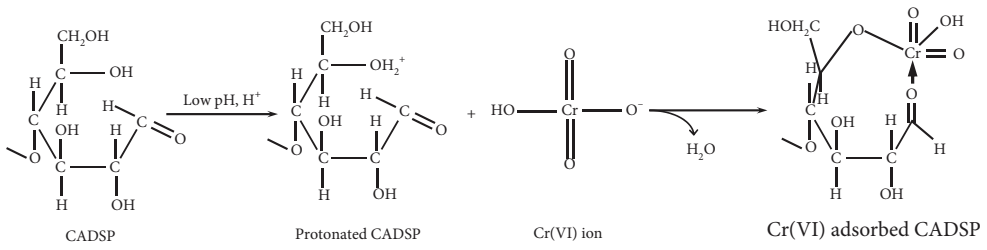


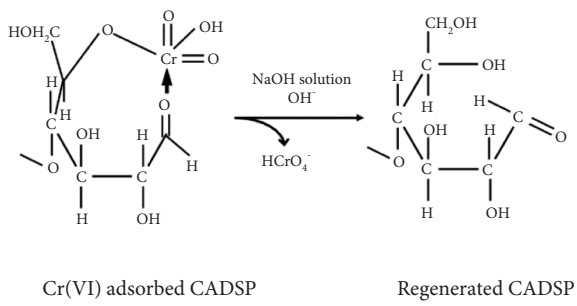
Figure 12: (a) Desorption percentage of Cr(VI) vs. concentration of NaOH, and (b) fluctuation in the adsorption capacity of CADSP during the subsequent cycle of adsorption and desorption.



Scheme 1: Mechanism of charring of RADSP to give CADSP [26, 60].



Scheme 2: Mechanism of Cr(VI) biosorption on CADSP.



Scheme 3: Mechanism of desorption of Cr(VI).

disturbing the chemical stability of the adsorbent. Hence, the effective adsorption capacity with good Cr(VI) ions recovery and reusability is shown by the CALS.

3.9. Cr(VI) Biosorption/Desorption Mechanism. The surface area of the adsorbents is increased by the ring-opening of the RADSP cellulose units during the charring process, which also increases the active sites on the surface of the adsorbents. Scheme 1 depicts the chemical pathway for the synthesis of CADSP from RADSP.

In Scheme 2 illustrates the mechanism of Cr(VI) biosorption on CADSP. Since $HCrO_4^-$ is the main form of Cr(VI) at optimal pH 2, the solution at this pH contains a significant number of H^+ ions. The process of surface protonation causes the biosorbent to have a positively charged surface. As a result, $HCrO_4^-$ is electrostatically attracted to the protonated surfaces of the biosorbents, which causes it to bind to the surface of CADSP. Additionally, Cr(VI) might be adsorbed onto protonated sites of -OH within the CADSP by an ion-exchange mechanism. Additionally, an ion-exchange process may allow Cr(VI) to be adsorbed onto protonated sites of - OH inside the CADSP [61].

NaOH solution can be used to regenerate biosorbent and recover Cr(VI) ions that have been consumed by the adsorbent. According to Scheme 3, hydroxyl ions present in solution exhibit ligand replacement reaction with the sorbed oxyanions of Cr(VI) [45, 62].

4. Conclusions

The biosorption study of a biosorbent made from *A. donax* stem powder revealed that CADSP can effectively remove Cr(VI) from water by the process of biosorption. XRD examination revealed that the adsorbent's crystallinity is amorphous, while SEM and EDX revealed the rough and porous surfaces are present in CADSP, which are filled in Cr-adsorbed CADSP. The pH_{PZC} of CADSP was determined to be 4.0 and the adsorbent showed the best biosorption at a pH value of 2. With a maximal biosorption capacity (q_m) of 76.92 mg/g at optimal pH, Cr(VI) was fitted into the Langmuir biosorption isotherm and pseudo-second-order kinetic models. The desorption of Cr(VI) from Cr-adsorbed CADSP was carried out with varying doses of NaOH as the eluent. According to the findings of this study, *A. donax* stem powder can be used to make an effective and inexpensive biosorbent for eliminating Cr(VI) from water and wastewater.

Data Availability

The data used to support the findings of the study are available from the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Krishna Prasad Bhattarai and Bishnu Datt Pant Contributed equally to this work.

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