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Biosorption of Cr(III) from aqueous solution using an agricultural by-product jute stick powder: Equilibrium and kinetic studies

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ABSTRACT

The adsorption capacity of chromium(III) from synthetic waste water solution by a low cost biomaterial, Jute Stick Powder (JSP)was examined. A series of batch experiments were conducted at different pH values, adsorbent dosage and initial chromium concentration to investigate the effects of these experimental conditions. To analyze the metal adsorption on to the JSP, most common adsorption isotherm models were applied. To study the reaction rate, the kinetic and diffusion models were also applied. The morphological structure and variation of functional groups in the JSP before and after adsorption was examined by scanning electron microscope (SEM) and Fourier transform infrared spectrometry (FT-IR). Maximum chromium removal capacities of JSP was 84.34%with corresponding equilibrium uptake 8.4 mg/g from 50 mg/L of synthetic metal solution in 60 minutes of contact time at pH = 6.0 and 28 °C with continuous stirring at 180 rpm. The percent sorption of the biomass decreased with increasing concentration of metal ion but increased with decreasing pH, increasing contact time and adsorbent doses. Data for this study indicated a good correspondence with both isotherms of Langmuir and Freundlich isotherm. The analysis of kinetic indicated that Chromium was consistent with the second-order kinetic adsorption model. The rate of removal of Cr(III) ions from aqueous solution by JSP was found rapid initially within 5-30 minutes and reached in equilibrium in about 40 minutes. The investigation revealed that JSP, a low cost agricultural byproduct, was a potential adsorbent for removal of heavy metal ions from aqueous solution.

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1. Introduction

Pollution created by heavy metal ions is dangerous to human health and environment. Ongoing industrialization is for the betterment of the human kind and human society is being developed by the use of increasing order of new products. Uncontrolled effluent treatment and mismanagement of waste disposal system is causing pollution in water body. Therefore, aquatic lives and surrounding ecosystem is adversely affected by the toxicity of harmful heavy metal ions. These toxic pollutants are entering into the human body through food chain and remain persistently. Bioaccumulation of heavy metal ions causes severe health problems in human body. Chromium is well known toxic heavy metal when it exceeds the tolerance limits although small amount of chromium is essential for animal and human health. Cr (III) and Cr(VI) are the species usually encounter in the environment. Among the chromium compounds trivalent is potentially harmful but hexavalent chromium has a greater risk due to its carcinogenic properties. Hexavalent chromium, which is primarily present in form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) poses significantly higher levels of toxicity in comparison with other valence states [1]. Researchers have reported that exposure to certain level chromium creates fatal diseases such as lung cancer, chrome ulcers, nasal septum perforation, as well as brain damage, renal dysfunction, hypertension, bone lesions, cancer, etc. [2]. The main industrial sources of chromium metal are leather tanning, paints and pigments, mining, electroplating, battery, smelting, alloy manufacturing, steel fabrication, plastic [3]. A number of conventional methods including ion exchange, reverse osmosis, electrochemical treatment, chemical precipitation, adsorption and so on are practiced for the removal of toxic heavy metals from aqueous solution. However, these methods have some drawbacks due to cost and management of sludge as a secondary pollutant. In recent years, adsorption especially biosorption process has gained great attention for the removal of heavy metal ions because it is very effective, versatile, powerful, most efficient, low cost and environment friendly. To remove heavy metal ions from wastewater an abundant, inexpensive and efficient agricultural by-products has become most popular [4]. For the removal of heavy metal Cr(III) ions from water and wastewaters a number of agro-based biomaterials were used such as peanut shells[5], *Lathyrus sativus* husk [6], soybean meal waste[7], *Nauclea diderrichii* seed biomass [3]. The present study focuses the use of an

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agricultural by-product *Jute Stick* which is left unused after separation of Jute fiber. Usually, they end up as fuel for earthen stoves or as fences for betel leaf plantations. Now a day small amounts are used for producing charcoal. Bangladesh is currently the second largest producer of jute fiber and producing nearly 30 lakh tones jute sticks every year. As a by-product Jute sticks are produced in extensive quantities. Therefore, JSP may be used as a cost effective potential biosorbents for the removal of toxic heavy metals and may affect the agricultural economy of the country. However, literature survey has shown that there is currently a less of information concerning the use of Jute Stick Powder (JSP) for biosorption purpose. Subhan *et el.* [8] removed arsenic from dirking water and organic dye was removed from industrial waste water using JSP reported by some researchers [9,10]. In the present study a triumph was taken to remove heavy metal ions Cr(III) from waste water using JSP without any treatment, as an example of low cost potential biosorbent under different experimental conditions in order to optimize the efficiency of the adsorption phenomena. For a better understanding of the adsorption performance equilibrium isotherm models and kinetic models were justified.

2. Experimental

2.1. Preparation of solutions

Analytical reagent (AR) grade chemicals were used in experimental. Stock solution of 1000 mg/L of Cr(III) was prepared by dissolving 3.046 g of $CrCl_3$ in one liter of double distilled water. Necessary solutions were prepared by further dilution of stock solution with distilled water. The range of concentrations of metal ions prepared from standard solution varies between 20 and 50 mg/L. Using 0.1 M NaOH or 0.1 M HCl solution, the pH of each test solution was adjusted to the required value before adding of adsorbent.

2.2. Collection and preparation of adsorbents

Fresh Jute Sticks were collected from agricultural firm located at Nawabgonj Upozila in Dhaka, Bangladesh. The jute sticks were chopped into small pieces and then were extensively washed in running tap water to remove dirt and then washed with distilled water three times, and left to air dry for some time to remove free water from the surface. After that it was transferred to the oven at 60 °C for 24 hours. This was powdered by grinding in a mechanical blender and sieved. The 80-100 mesh size fractions were stored in an air-tight container for experimental uses.

In order to identify the possible functional groups involved in the Cr(III) biosorption process raw biosorbents and metal-loaded biosorbents were analyzed using a FTIR spectrophotometer (IRPrestige-21, Shimadzu, Japan). Before pressed into a disk under high pressure, the dried biosorbents were grinded sufficiently with KBr at a ratio of 1:200 in an agate mortar. The spectra were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Scanning electron microscopy (JSM-7500F, Japan) was used to survey the surface morphology of the JSP biosorbent before and after biosorption of Cr(III) from water solution[11].

2.3. Batch biosorption experiment

Biosorption studies were carried out to investigate the effect of initial metal ion concentration, amount of biomass, shaking (reaction) time, solution pH. Sorption experiments were carried out in 250 mL conical flask. Solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH. The volume of metal ion solutions was 100 mL, the amount of biomass was 0.5 g, and the temperature was 28 °C. A sorption study with batch method was carried out by orbital shaker. After the sorption step, the biomass was separated from the solution using Whatman filter paper. Finally, the solutions were analyzed by flame atomic absorption spectrometry (FAAS). Effect of pH was investigated by undergoing metal adsorption at different pH values ranging from 2-8 keeping other parameters constant. Using initial Cr(III)concentration varied from 20 to 100 mg/L the effect of initial metal concentration was determined. In experiments concerning the effect of adsorbent dose, a range of JSP biosorbent samples (0.25, 0.50, 0.75 and 1.0 g/100 mL) were used. For contact time experiments, the procedure was similar with those presented above, with the difference that the phases were separated after a determined period of contact time.

The amount of adsorbed (mg/g) was calculated using the formulae in Equation (1).

$$q_e = \frac{V\left(C_0 - C_e\right)}{m} \tag{1}$$

The removal efficiency was determined by computing the percentage sorption using the formulae in Equation (2).

$$Sorption\left(\%\right) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where, q_e is the equilibrium adsorption capacity (mg/g); C_0 and Ce, the initial and equilibrium metal concentrations in the water (mg/L), respectively; V, volume of used water (L); and m, the mass of used bio-adsorbent (g).

2.4. Optimization of adsorption parameters

2.4.1. Effect of pH

pH of solution has been identified as the most important variable governing metal ions uptake because it influences the ionization of functional groups at the surface of a sorbent and hydrogen ions themselves may compete strongly with the adsorbates [12]. In this study, experiments for biosorption of Cr(III) on to jute stick powder was carried out variation of pH from 2 to 8. The Figure 1 shows that the "adsorption (%) *vs.* pH" plots revealed that the amount of Cr(III) adsorbed has increased from 23.334 to 84.336% by increasing pH of solution from 2 to 6 and reached a plateau at pH = 6. After this pH, the change in the sorption percentage was not very significant. Hence, the maximum sorption of Cr(III)by JSP could only be obtained after a pH of 6.0. The increase in metal removal as the pH increases can be explained on the basis of decrease in competition between protons and metal cations for the same binding sites [13]. Above the value of pH = 6, Cr(III) ions might be precipitated as $Cr(OH)_3$ resulting the decreasing the adsorption [14]. To avoid metal precipitation, the whole experiments were conducted between pH = 6.0-6.5. As the pH of prepared medium with distilled water was very close to 6.0, there were no practical pH adjustments for all the experiments. Therefore, the experimental processes became environment friendly [15].

2.4.2. Effect of contact time

The rate of biosorption is important for designing batch biosorption studies. Consequently, the effect of contact time on the biosorption of Cr(III) was investigated in this study. The effect of contact time on the adsorptive removal of Cr(III) at 28 °C for a range of concentrations (20-100 mg/L) of Cr(III) metal ions is shown in Figure 2, which reveals that the rate of sorption of chromium on jute stick powder was rapid, with 60-70% of Cr adsorption occurring within the first 30 min and attaining equilibrium was at 40 min. in all cases and the percent uptake of metal ions increased rapidly to 93.03%in equilibrium time for 20 mg/L of Cr(III).

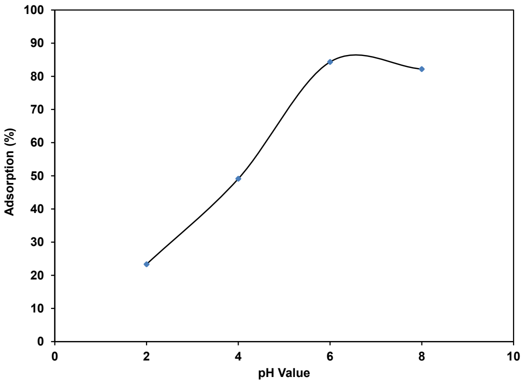

Figure 1. Effect of pH on Cr(III) biosorption onto JSP (Co = 50 mg/L; Dose = 0.5 g/100 mL).

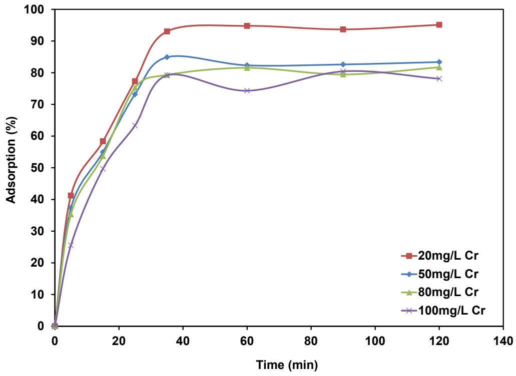

Figure 2. Effect of contact time on Cr(III) biosorption in % adsorption with the increase of time. (Co = 50 mg/L; dose = 0.5 g/ 100 mL).

This behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the sorbent. The adsorption process of Cr(III) suggests that the binding may be through interactions with functional groups located on the surface of jute stick powder. According to these results, the agitation time was fixed as 60 min for the rest of the batch experiments to make sure that equilibrium was attained. From the experimental results it is observed that further increase of time there was no significant increase of biosorption, this is because there is saturation of the active sites on the biomass and leading to a repulsive force between the adsorbate and adsorbent [16].

2.4.3. Effect of initial metal ion concentration

The extent of removal of heavy metals from aqueous solution depends strongly on the initial metal ion concentration. According to Figure 3a, the results demonstrate that at a fixed adsorbent dose, the percentage of adsorption decreased with increasing concentration of solution. The Jute stick powder as a biomaterial contains several functional groups which play a role in the sorption process. The number of available functional groups decreases with the increase in the initial metal ion concentration and this is confirmed by the decrease in the percentage sorption with an increase in the initial metal ion concentration, although the amount of adsorbed metal increases in the meantime. At higher concentrations more Cr(III) ions are left unadsorbed in solution due to the saturation of binding sites at a fixed dose (0.5 g). The Figure 3a discloses that the removal of Cr(III) by Jute stick powder decreased from 93.03 to 79.14% when the concentration increased from 20 mg/L to 100 mg/L. On the contrary, adsorption capacity for each gram adsorbent is increased gradually from 3.72 to 15.83 mg/g with the incensement of concentration (Figure 3b). This result can be explained as at lower concentrations, the ratio of number of metal ions to the available sorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration. At higher concentrations, however, the available sites of adsorption become fewer and subsequently the removal of metals depends on the initial concentrations. Hence, the removal of Cr(III) metal depends on the initial metal ions concentrations and decreases with increase in initial metal ions concentration.

2.4.4. Effect of adsorbent doses

The adsorption mainly depends upon the available surface area which is confirmed by the adsorbent quantity. Keeping other parameters constant dosage of JSP were varied from 0.25 to 1.00 g in 100 mL of solution to observe the removal of Cr(III) ions. Figure 4a shows that the percent removal of Cr(III) ions was increased with the incensement of the adsorbent amount and maximum removal (88.45%) was attained with the dose of 1.0 g. This is because the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [17]. Further increase in the dose may not significantly change the biosorption percentage due to the particle interactions, such as aggregation, resulting from high sorbent concentration leading to a decrease in the total surface area of the sorbent. The results found are close agreement with the result disclosed by authors described in literature [18]. On the other hand, Figure 4b depicts that uptake capacity or amount of metal adsorbed (q, mg/g) decreased with the increase of the biosorbent dose. This may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process.

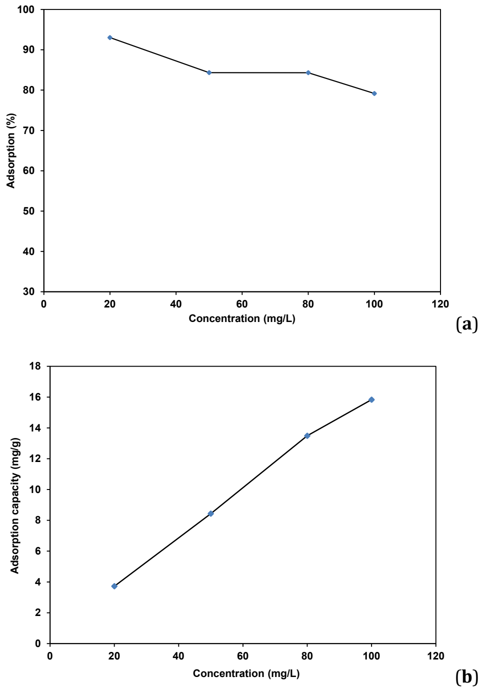

Figure 3. Effect of initial concentrations of Cr(III) (**a**) percent removal and (**b**) adsorption capacity (mg/g) by jute stick powder.

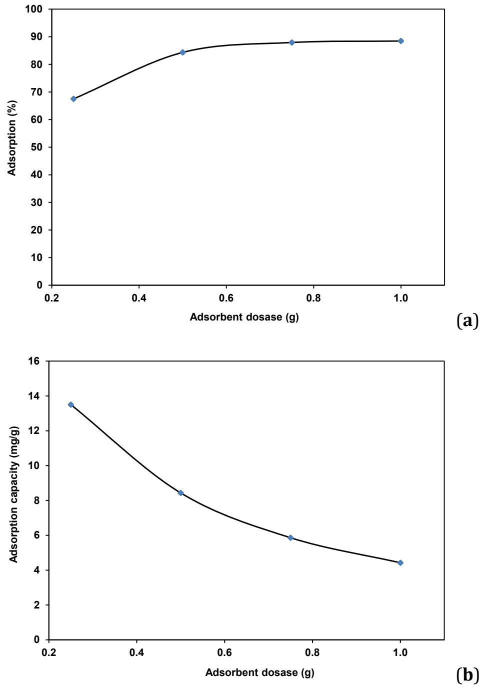

Figure 4. Effects of different doses on the removals of Cr(III) from water by jute stick powder. (**a**) Percent removal; (**b**) Adsorption capacity.

The amount of unsaturated active sites was increased with the increase of dose of JSP. Hence, there was an insufficiency of metal ions in the solution with respect to available binding sites in JSP biosorbent.

2.4.5. Effect of shaking speed

Figure 5 indicates that the percentage biosorption increases when agitation speed increased, obtained at peak and then drops to lower values at higher speed. It resulted a maximum 73.98% Cr(III) biosorption at 180 rpm. The batch biosorption performed higher removal at different shaking speeds, so a value of around 180 rpm was employed as standard for other experiment. At low and high speeds, percent removal of Cr(III) was found less because, low speed could not spread the particles properly in the water by providing active binding sites for biosorption of metal ions. It resulted in an accumulation of JSP in the bottom of water and it buried the active binding sites.

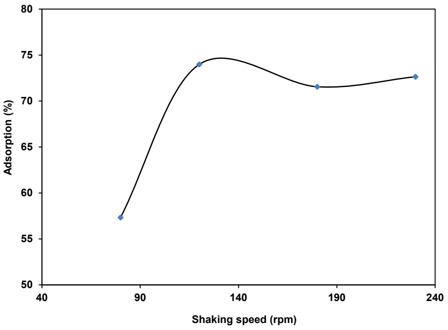

Figure 5. Effect of shaking speed on removal of Cr(III) by jute stick powder. (Co: 50 mg/L; d: 0.5 g; t: 60 minutes: pH= 6; T = 28 °C).

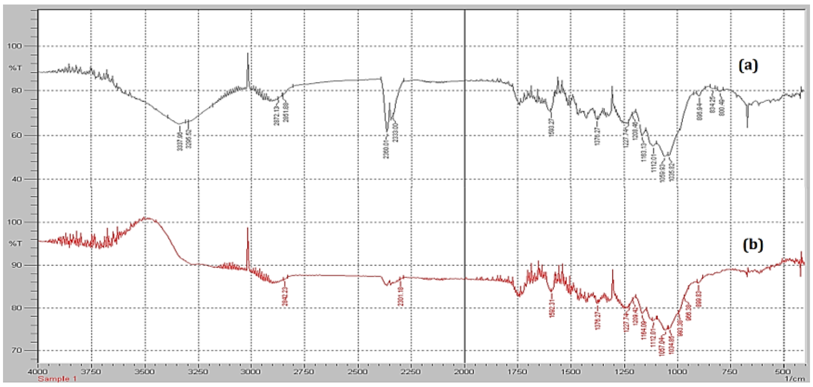

Figure 6. Comparison of FTIR spectra of (a) raw JSP and (b) Cr(III) loaded JSP.

However, there is a lack of sufficient time to bind with metal ions in the condition of vigorously spreading of the particles of biosorbent JSP [19].

3. Results and discussions

3.1. Characterization

3.1.1. FT-IR studies

FTIR spectroscopy method was applied to determine the functional groups present in JSP. The preliminary quantitative analysis of major functional groups present in JSP is shown by the Figure 6a. The Figure 6b represents the change of spectral pattern due to stretching and bending of active groups present in the JSP after adsorption of Cr(III). FTIR experiment for raw and Cr(III) loaded JSP were conducted in same conditions. It is assumed that for the O-H stretching vibrations a broad and intense adsorption peak was found at 3337 cm^{-1} due to presence of H-bonded –OH groups in the water adsorbed adsorbents. The peaks observed at 2900 – 2851 cm^{-1} can be attributed to the C–H stretching vibrations of methyl, methylene and methoxy groups. Peak observed at 1745 cm^{-1} is the stretching vibration of C=O bond due to non-ionic carboxyl groups (COOH, –COOCH$_3$) and may be assigned to carboxylic acids or their esters [20]. The two sharp bands in the region 1593 and 1506 cm^{-1} are most probably due to stretching modes of benzene ring [21] of lignin present in JSP. The band at 1376 cm^{-1}, which is ascribed to the C–H deforming (symmetric), may be attributed to lignin, α -cellulose, or xylan. Also 1163 cm^{-1} peak represents C–N bond. The band at 1036 cm^{-1}, which is assigned to aromatic C–H in plane and C–O for primary alcohol in lignin, was found in raw JSP [22]. However, peaks 2330 and 2360 cm^{-1} in the spectrum might be due to noises obtained for flaws in the machine. Carboxyl and hydroxyl groups were present abundantly in the lignin, hemicelluloses and α-cellulose of JSP and these groups act as proton donors resulting deprotonated hydroxyl and carboxyl groups which may be involved in coordination with metal ions [23]. It was observed a board intense peak at the region 3337 cm^{-1} due to –OH stretching band likely to become less intense for the Cr(III) loaded JSP surface because –OH groups are bonded with metal ion. FTIR spectra of metal Cr(III)adsorbed JSP showed that the peaks expected at 2872, 1593 and 1055 cm^{-1} (Figure 6a) had shifted, respectively, 2842, 1592, and 1050 cm^{-1} due to Cr(III) ions biosorption (Figure 6b). These shifting may be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, are predominant contributors in metal ion uptake [24]. These data are in nearly close agreement with the results found by other researchers experienced with characterization of JSP [25].

3.1.2. Scanning electron micrographs (SEM) analysis

The surface structure of Jute Stick Powder was examined by SEM. Figure 7 represents the SEM micrograph which revealed some significant feature of the structure. JSP without metal loaded and after metal loaded was taken for SEM analysis. The initial structure of the JSP (Figure 7a and b) reveals the combination of small and large particles, heterogeneous rough and porous surfaces. Textured and porous surfaces are found on the JSP which was expected to promote the uptake of metal ions. For an effective adsorption high surface area and pore structure are required. Surface area increases with the incensement of porosity. From Figure 7c and it is observed that the thread- nodule like particles with irregular porous surface area loaded metal ions. Thus, it is presumed that, there is a good possibility for a metal to be trapped and adsorbed into the binding sites of the surface.

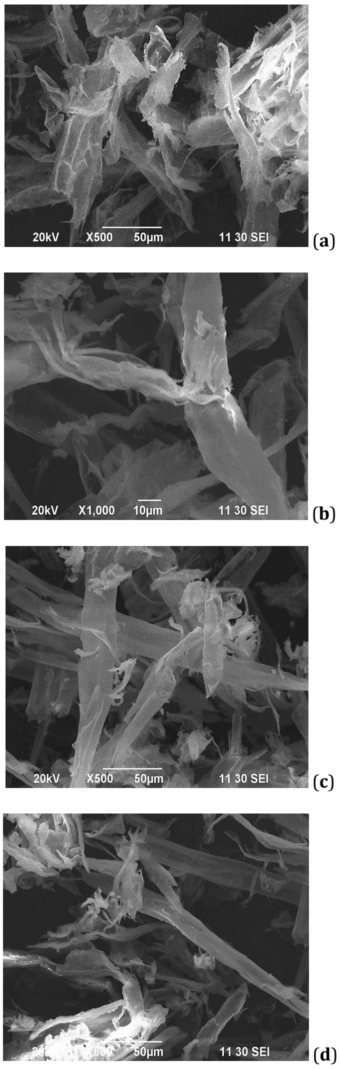

Figure 7. SEM images of JSP (**a**, **b**) before and (**c**, **d**) after Cr(III) adsorption.

3.2. Adsorption isotherm

Adsorption equilibrium isotherms are basic requirements for designing any adsorption system. The adsorption isotherm indicates how the adsorbate distributes between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The adsorption data has been analyzed with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [26]. At the equilibrium of an adsorption process, adsorption isotherm is suitable in describing the distribution of adsorbate molecules between the liquid and the solid phase.

3.2.1. Langmuir isotherm model

The Langmuir isotherm is used for monolayer adsorption onto a surface containing a finite number of identical binding sites. Based upon these assumptions, Langmuir [27] represented the following Equation (3),

$$qe = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

Langmuir adsorption parameters were determined by transforming the Langmuir Equation (3) into linear form.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \tag{4}$$

where, K_L is Langmuir isotherm constant (L/mg) related to the affinity between the sorbent and the sorbate and q_m is the maximum adsorption capacity (mg/g). Values of Langmuir parameters q_m and K_L were calculated from the slope and intercept of the linear plot of $1/q_e$ *vs* $1/C_e$ as shown in Figure 8a. Values of q_m, K_L and regression coefficient r^2 are listed in Table 1. These values for JSP biosorbent indicated that Langmuir theory describes the biosorption phenomena favorable [28]

An important characteristic of the Langmuir isotherm is expressed in a dimensionless constant equilibrium parameter R_L. The R_L value indicates the shape of the isotherm and is given in Equation (5).

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

Table 1. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich constants for Cr(III) bio-sorption by JSP.

Isotherm model	**q_{max} (exp.) (mg/g)**	**q_{max} (calc.) (mg/g)**	**K_L (L/mg)**	**R_L**	**r^2**
Langmuir isotherm	15.832	16.949	0.2006	0.047-0.199	0.975
Freundlich isotherm	-	-	**n (g/L)**	**K_F (mg/g)**	**r^2**
	-	-	1.824	3.04	0.981
Temkin isotherm	-	-	**B_T (J/mol)**	**A_T (L/g)**	**r^2**
	-	-	564.5541	1.429	0.923
Dubinin-Radushkevich isotherm	-	**q_m (mol/g)**	**K_D (mol^2/J^2)**	**E (J/mol)**	**r^2**
	-	12.603	7.00E^{-07}	845.3085	0.856

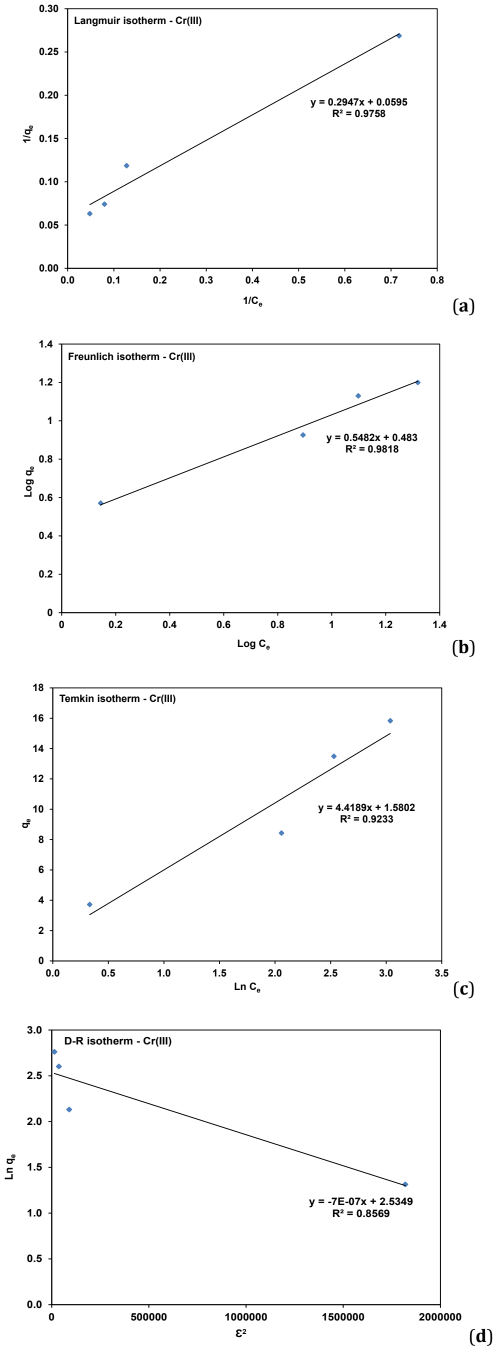

Figure 8. Adsorption isotherm models (**a**) Langmuir, (**b**) Freundlich (**c**) D-R and (**d**) Temkin for biosorption of chromium (III) by JSP (pH = 6.0, biosorbent dose concentration: 0.5 g/ 100 mL, contact time: 60 minute, temperature: 28 °C.

According to Mckay *et al.* [29], R_L values between 0 and 1 indicates a favorable adsorption process, 1 indicates a linear adsorption, 0 indicates irreversible adsorption, while an R_L value greater than 1 signifies an unfavorable adsorption process. This implies that the adsorption of metal ions on adsorbent is a favorable adsorption when the R_L values obtained at all initial concentrations in the range $0 < R_L < 1$.

This suggests the applicability of the biosorbent for metal removal. Table 1 shows that the R_L values were found to be 0.047-0.199 for concentration of 20-100 mg/L of Cr(III). They are in the range of 0-1 which indicates the favorable biosorption.

3.2.2. Freundlich isotherm model

Freundlich isotherm model is based on the assumption that adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. The sorption energy exponentially decreases when sorption occurs completely of an adsorbent. It is an empirical model equation which can be used to describe heterogeneous systems. It is expressed by the following equation [30].

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

The above equation can be rearranged to the following linear form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{7}$$

where, K_F is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of log q_e versus log C_e as shown in Figure 8b. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.824 for JSP, shown in Table 1. Since n lie between 1 and 10, this indicates the physical biosorption of Cr(III) onto JSP. According to Kadirvelu *et al.* [31], the value of *n* between 1 and 10 represents a beneficial adsorption process. The value of the regression coefficient (r^2) from the isotherm curve gives the information that experimental data better fit with the model.

3.2.3. Temkin isotherm model

The Temkin isotherm model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage and applicable in medium value of concentration [32]. The expression of equation for a uniform distribution of binding energies(up to some maximum binding energy)is defined by the Equation (8)

$$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e \tag{8}$$

where, A_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is the Temkin isotherm constant, R is the universal gas constant (8.314 J/mol.K) and T is temperature at 301K.These constants were obtained from plotting q_e versus ln Ce, Figure 8c. Values of b_T and K_T are listed in Table 1.

3.2.4. Dubinin-Radushkevich (D-R) isotherm model

The D-R isotherm model is a semi-empirical equation based on Polany's adsorption potential theory where adsorption follows minipore filling theory represent multilayer character, involves van der Waals forces. The model is applicable for physical adsorption processes and the linear form is expressed as [33].

$$\ln q_e = \ln q_m - K_D \varepsilon^2 \tag{9}$$

where, q_m and K_D are the constants of D-R isotherm model represents the maximum adsorption capacity (mol/g) and the adsorption energy, respectively, and ε is the Polanyi potential which is defined as:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

The constant K_D is related to the mean free energy of sorption per mole of the adsorbent as it is moved from infinite distance in the solution to the surface of the biosorbent, E, which can be calculated using the following relation:

$$\mathrm{E} = \frac{1}{(2K_D)^{\frac{1}{2}}} \tag{11}$$

The values of q_m and K_D were obtained from the slope and the intercept of ln q_e versus ε^2 plot, Figure 8d and represented in Table 1.

3.3. Adsorption kinetic model

The kinetics of biosorption is essential to determine the efficiency of the sorbent. Kinetic models have been applied in experimental data to predict the biosorption kinetics. Lagergren's pseudo-first order, McKay and Ho's pseudo-second-order and Weber and Morris's intra-particle diffusion models were used to describe the dynamic adsorption process [34].To obtain the kinetic data metal uptake capacity (qt, mg/g) was calculated by the following mass balance equation.

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{12}$$

where C_0 and C_t are Chromium concentrations (mg/L) at time 0 and t, respectively, V is the volume of the solution (L), and m is the mass of JSP (g).

The linear form of the pseudo – first order equation of Lagergren [35] is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{13}$$

where, q_e (mg/g) and q_t (mg/g) are the adsorption amount at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the rate constant in the pseudo-first-order adsorption process. The pseudo first order rate constant values were calculated from the slope and intercept, Figure 9a. The calculated values and their corresponding linear regression correlation coefficient values are shown in Table 2. The correlation coefficient value was found to be 0.912, which shows that this model cannot be applied to predict the adsorption kinetic model. Furthermore, the equilibrium biosorption capacities (q_e, cal) inferred from the pseudo first-order model were likewise not in good agreement with the experimentally determined values (q_e, exp), Table 2.

Based on the adsorption capacity at equilibrium the pseudo-second-order equation can be expressed by the following Equation [36].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

where k_2 (g/mg/min) is the rate constant of the second-order equation. k_2 and q_e were obtained from intercept and slope of the plot of t/q_t *vs* t, Figure 9b.

The pseudo-second order rate constant k_2, the calculated q_e value and the corresponding linear regression correlation coefficient value are given in Table 2. At all initial Chromium concentrations, the linear regression correlation coefficient r^2 values were higher value which confirms that the adsorption data were well represented by pseudo-second order kinetics

Table 2. Bio-sorption kinetic model parameters for Cr(III) by JSP.

Kinetic model	**q_e, exp. (mg/g)**	**q_e, calc. (mg/g)**	**k_1 (min^{-1})**	**r^2**
Pseudo-first order	8.43	6.87	0.062	0.921
Pseudo-second order	**q_e, exp. (mg/g)**	**q_e, calc. (mg/g)**	**k_2 (g/mg/min)**	**r^2**
Intra-particle diffusion	-	**K_{id} (mg/g.$min^{-0.5}$)**	**C (mg/g)**	**r^2**
	-	1.508	0.202	-

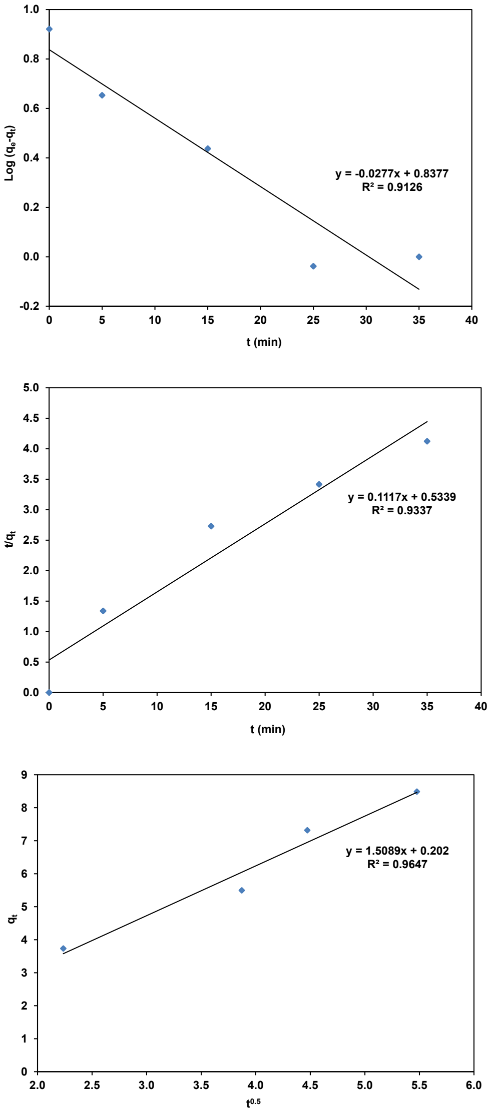

Figure 9. Adsorption kinetic models (**a**) pseudo-first-order equation, (**b**) pseudo-second-order equation, (**c**) Weber and Morris intra-particle diffusion equation, for biosorption of Cr(III) by JSP (pH = 6.0, biosorbent dose concentration: 0.5 mg/100 mL, Cr(III) concentration: 50 mg/L, temperature: 28°C)

and predicts the adsorption is due to chemisorptions. Moreover, the q_e, (cal.) values calculated from the pseudo second-order model matched the q_e (exp.) values closely.

The theory proposed by Weber and Morris [37] is established as intra-particle diffusion model. This equation is expressed as

$$q_t = K_{id} t^{0.5} + C \tag{15}$$

where k_{id} (mg/g.$min^{-1/2}$) is the rate constant of intra-particle diffusion, q_t (mg/g) is the amount of metal ion adsorbed at time t, C (mg/g) is the intercept.

A plot between q_t *vs* $t^{0.5}$ for Cr(III) biosorption onto jute stick powder is shown in Figure 9c. From the Figure 9c, it is revealed that all plots are linear. The parameters K_{id}, C and r^2 are summarized in Table 2. In this study, a linear plot was obtained that did not pass through the origin (Figure 9c), suggesting that intra-particle diffusion was not the sole rate-determining step [38]. In the adsorption mechanism the rate-limiting reaction is controlled both through film diffusion and intra-particle diffusion.

3.4. Regeneration and reuse of biosorbent

The regeneration of biosorbents involved in reducing the operating cost in industrial application. In the present study for the recovery of Cr(III) from loaded-JSP four desorbing agents such as distilled water, 0.1 M HCl, 0.1 M HNO_3, 0.1 M NaOH were used.

Table 3. Cr(III) metal ion adsorption capacities on various adsorbent materials.

Adsorbent	Initial metal concentration (Co, mg/L)	Adsorbent loading	q_{max} (mg/g)	References
Naucleadiderrichii seed	1000	100 mg/50 mL	483.81	[3]
Wheat straw	300	5 g/L	20	[39]
Streptomyces sp. (MB2)	50	2 mg/100 mL	2.89	[40]
Modified Rosa gruss an *teplitz* (Red rose)	100	2 g/100 mL	45.03	[41]
Jute stick powder	100	0.5 g/100 mL	15.83	Present study

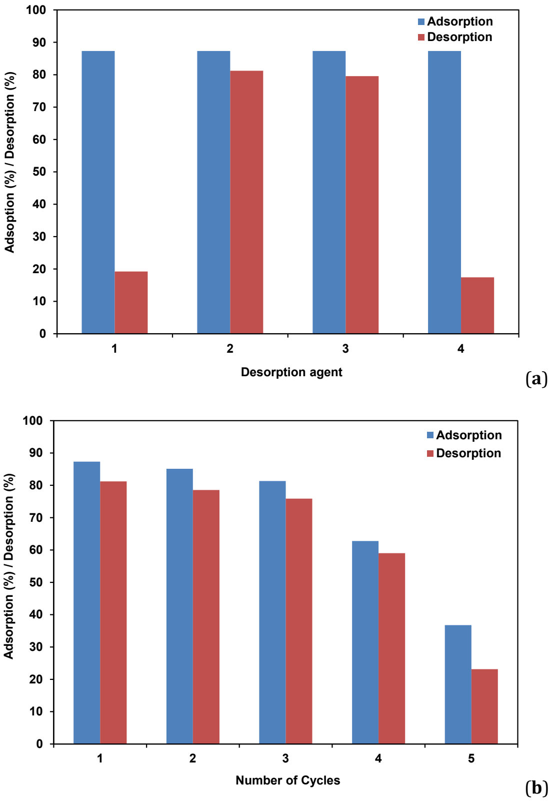

Figure 10. (**a**) %Desorption by four desorbing agent, (1) distilled water, (2) 0.1 M HCl, (3) 0.1 M HNO_3 and (4) 0.1 M NaOH; (**b**) Five adsorption and desorption cycles by best desorbing agent 0.1 M HCl.

The batch results of adsorption and desorption with four eluents plotted in Figure 10a shows the maximum desorption gained by 0.1 M HCl amounted by 81.23% whereas lowest amount, 17.43% desorbed by 0.1 M NaOH. Reuse and further applicability of biosorbent was tested by conducting five successive adsorptions and desorptions cycles (Figure 10b), first three of which remain almost unchanged amount. For the fourth and fifth cycles adsorption and desorption became less. Therefore, biosorbent JSP can be use more than three times with a small efficiency loss for biosorption of Cr(III).This results indicate that the mechanism of biosorption of Cr(III) on to JSP is an ion exchange.

4. Conclusion

Jute Stick Powder was found to be an effective biosorbent for the removal of Cr(III) ions from aqueous solutions. The results suggest that pH, doses, initial Cr(III) ion concentration, contact time and shaking speed affected the biosorption process. Quick equilibrium time reached at 40 min for maximum removal of Cr(III) poses practical potentiality of Jute Stick Powder as an efficient metal adsorbent. The maximum monolayer uptake capacity of JSP was found to be 15.83 mg/L of Cr(III) in each gram of JSP from 100 mg/L of metal solution (Table 3). Langmuir and Freundlich adsorption isotherm could be used to describe adsorption isotherm but the Langmuir isotherm was found to be in good agreement with experimental data. The kinetic results provided the best correlation of the experimental data of biosorption of chromium(III) onto JSP by pseudo second-order equation. Characterization of the JSP biosorbent with FTIR showed that it possesses hydroxyl and carboxylic groups which is likely the main biosorption site for Cr(III). The multilayer sorption of Cr(III) occurs on the homogeneous surface confirmed by SEM images. JSP biosorbent can be used repeatedly at least three times by desorbing Cr(III) ions. The results signifies that a locally available, low-cost agri-waste having high adsorption capacity Jute Stick may be used as an alternative adsorbent for removal of Cr(III) ions from waste water.

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Disclosure statement DS

Conflict of interests: The authors declare that they have no conflict of interest.
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Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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