Jute Stick Powder: A New Approach to Efficient Biosorbent for the Simultaneous Removal of Pb, Cr and Cd from Waste Water

Mohammad Nasir Uddin[a,*], Monir Uddin[a], Ibrahim Khalil[a], Jahangir Alam[a] and A.K.M. Atique Ullah[b]

[a]*Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh*
[b]*Analytical Chemistry Laboratory, Chemistry Division, Atomic Energy Centre Dhaka, Bangladesh Atomic Energy Commission, Dhaka-1000, Bangladesh*

Abstract

This research was aimed to evaluate the potential of biosorption technique in more realistic conditions that appeal to the industry by exploiting locally available biosorbents such as jute stick powder (JSP), an agricultural product, for the removal of toxic Pb(II), Cr(III) and Cd(II) ions from wastewater. Fourier transform infrared spectroscopy (FTIR) and Scanning electron micrographs (SEM) analysis proved that the surface of biosorbent was porous, with heterogeneous structures that contained high internal spaces. The removal efficiencies of the mixture of the target metals by JSP were optimized with respect to pH, initial metal concentration, shaking time and biomass dose. Biosorption performance of JSP in multiple metal systems was above 90 percent adsorption for tested metal ions. Biomass regeneration efficiencies up to 98% were achieved using acid as eluent. Sorption performance of the JSP as biosorbent was examined by classical adsorption equilibrium isotherms, kinetics in batch systems, and dynamic continuous flow studies. Batch sorption studies revealed that pseudo-first, pseudo-second-order, and Langmuir isotherm models were suitable to describe the metals sorption kinetics and equilibrium, respectively.

Keywords: Biosorption, jute stick powder (JSP), Pb(II), Cr(III) and Cd(II) ions, isotherm, wastewater

1. Introduction

Industrialization, dumping of waste at landfills and the rising human population have given rise to many human activities that cause land pollution [1]. A broad spectrum of hazardous substances contaminate the environment due to industrial discharge in the form of wastewater that contains industrial processed toxic heavy metals from electroplating, mining, metal finishing, leather tanning, metallurgy, electronics, fertilizers, chemical manufacturing and petroleum industries [2]. Some common heavy metals are lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe) and the platinum group elements. They are persistent

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* Corresponding author. Tel. : 008801710915011
E-mail: nasircu72@gmail.com, mnuchen@cu.ac.bd, ORCID: 0000-0003-1235-2081

Manuscript History:
Received 07 October, 2020, Revised 18 October, 2020, Accepted 19 October, 2020, Published 30 October, 2020

environmental contaminants because of they are non-degradable or cannot be destroyed naturally [3]. These industries discharge untreated waste in nearest water bodies that finally fall into the rivers. As a result, various refuse and disposable materials come from these industries, ships and oil tankers [4]. Heavy metals pose various acute and chronic disorders such as kidney damage, liver damage, gastrointestinal distress, nervous deterioration, pulmonary fibrosis, renal oedema, skin diseases, and cancer [5,6].

According to Ahmed *et al.* [7] the concentrations of some heavy metals in water, sediment and fishes exceeded the recommended value. Removal of toxic metals from industrial effluents to safe levels is an expensive process, although several competing technologies exist for such an operation. Over the last few decades, several methods have been used for the removal of heavy metals from water and waste water. The commonly used procedures for removal of heavy metals from contaminated waste water are chemical precipitation [8], electro-winning [9], ion exchange [10], ultra-filtration [11], reverse osmosis [12], carbon adsorption and phytoremediation. Searching for cost-effective and environmentally-sound means of toxic metal removal is a continuous need for the industries with wastewater effluent with metals.

Biosorption process has been known as an attractive and feasible alternative to physicochemical methods for removal of heavy metals from various wastewater streams and a multitude of biosorbents have been examined by researchers for their metal removal performances. Application of natural and abundant sorption material known as biosorbents comprising microbial biomass, agriculture waste and industrial waste biomass, has gained international attention in the scientific world as a low-cost and effective method for removal of heavy metals from aqueous solutions. In recent years, agricultural byproducts have been widely studied for metal removal from water. These include peat, wood, pinebark, bananapith, soybean and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves.

Jute dicotyledonous fiber-yielding plant of the genus *Corchorus*, order *Tiliaceae*, was once known as the golden fiber of Bangladesh, since it was the most important cash crop for the country. As a byproduct of jute, the jute stick fiber is cheap, easily available in extensive quantities,easily grown, and sometimes abandoned by jute cultivators. Besides, jute sticks are used to produce charcoal nowadays. Using this agricultural byproduct as a biosorbent to remove heavy metal ion from aqueous solution may affect the agricultural economy. Our objectives are to investigate the optimum sorption condition such as solution pH, contact time, initial metal ion concentration, adsorbent dose and shaking speed for maximum removal of Pb(II), Cr(III) and Cd(II) ions from aqueous solution. Necessary equilibrium isotherm model and equilibrium kinetics model are also justified to the experimental data to assess the adsorption quality and address the issues related to large scale applications of the process.

2. Methods and Materials

2.1. Chemicals and instrumentation

All the chemicals used were of analytical grade. The metal salts, $CrCl_3$,$[Cd(NO_3)_2.4H_2O]$, $Pb(NO_3)_2$ were purchased from BDH company. AR grade HCl, NaOH was used to adjust the solution pH. Deionized doubly distilled water was used throughout the experimental studies. An Atomic absorption spectrophotometer (AA7000, SHIMADZU), with Cr, Cd and Pb hollow cathode lamp and air acetylene flame, was used. A pH meter (HANNA, HI2209) was used for pH measurements. A mechanical orbital shaker (Stuart, Orbital shaker, SSL1) was used for agitating the samples. Fourier transform infrared spectrometry (IRPrestige-21, SHIMADZU, Japan) was used to analyze the functional groups in Jute stick powder when the spectrum was corrected for a KBr background.

2.2. Collection and characterization of biosorbents

Fresh Jute Sticks were collected from an 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. After that it was transferred to the oven at 100 °C for 24 hours. Dried Jute stick was crushed, milled into powder, sieved into uniform size 22 meshes and stored in an air-tight container for experimental uses. The Jute Stick Powder (JSP) was characterized by Fourier transform infrared spectroscopy (FTIR).

2.3. Preparation of stock solution

1.598g of $Pb(NO_3)_2$, 3.046g of $CrCl_3$, and 2.751g of $Cd(NO_3)_2.4H_2O$ were dissolved in one liter of double make a tertiary solution of concentration of 1000 ppm. Further dilution as required was done with distilled water.0.1M HCl and 0.1M NaOH solution was prepared to adjust the pH.

2.4. Batch biosorption experiment

Biosorption studies were carried out in 250 mL conical flask to investigate the effect of initial metal ion concentration, amount of biomass, shaking (reaction) time, solution pH, reaction temperature, and successive loadings. Experimental parameters such as shaking time of 60 min at 180 rpm, the amount of biosorbent 0.5 g, the solution volume 100.0 mL, and the metal ions concentration 50 ppm at room temperature (28 ºC) were optimized as standard.

The amount of adsorbed (mg/g) was calculated using the formulae below.

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

where, q_e is the equilibrium adsorption capacity (mg/g); C_0 and Ce, the initial and equilibrium metals concentrations in the water (mg/l), respectively; V, volume of used water (l); and m, the mass of used bioadsorbent (g).

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

$$\%\, Sorption = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

2.5 Collection and experimental works of industrial waste water

Among four industrial waste water samples, two were collected from Eastern Refinery, a crude oil refinery factory, while the remaining two samples were collected from TSP complex limited, a fertilizer manufacturing factory. At first, water was filtrated and insoluble components were removed. Initial concentration of dissolved metal ions present in waste water was determined by atomic absorption spectroscopy (AAS). Another portion was taken in a conical flask and JSP was added experiment as 2.6 was followed. Then percentage of adsorption and adsorption capacity was calculated.

Data assimilation and plotting in curve were done by using Microsoft excel in a good precision. All the parameter and constant of isotherm model and kinetic model were calculated from the curve and assessed with necessary figures and tables.

2.6. Regeneration of the biosorbent

Four types of solvents which were distilled water, 0.1M HCl, 0.1M HNO_3 and 0.1M NaOH were tested for regenerate biosorbent JSP for further application. The 0.5g loaded JSP was taken in 100mL of above solvent and shaken for 60 min at 180 rpm in room temperature (28°C). The regenerated biosorbent was washed with distilled water and used for the next adsorption cycle.

2.7. Optimization of experimental conditions

100 mL of 50 ppm tertiary stock solution were transferred into 4 conical flasks of 250 mL. The initial pH of the samples was adjusted to various values in the range of 2 to 8.0 and each sample was adjusted using either 0.1M HCl or 0.1M NaOH. The optimum pH for maximum metal adsorption was selected by atomic adsorption spectrometer.

To investigate the dose effect, different doses of JSP within 0.25g-1g were added to each conical flask containing 100 mL of 50 ppm tertiary metal solution at pH 6-6.5and shaken at 180 rpm for 60 minutes. The contents were allowed to settle for 5 minutes and then filtered. Residual metal concentration was estimated and dose for maximum adsorption was selected.

The experimental procedure was followed to check the effect of contact time at specified intervals between 30-120 minutes and optimum contact time was selected by analyzing for residual concentrations of metals.

The experiment was repeated at the optimum pH, doses and contact time taking different concentration metals from 20-70 ppm and the optimum initial metal concentration was identified.

Studies on the experiment were conducted to select the effect of stirring rate on the adsorption of metals by varying speeds of 80-230 rpm when test optimum conditions remained the same. The optimum stirring rate was selected analyzing the residual metal ions.

2.8. Validation methods

2.8.1 Adsorption equilibriums studies

The experiment for equilibrium isotherm for adsorption of metals onto JSP was carried out at different initial concentration of metals (20-100 ppm) at optimum experiment conditions. Adsorbed metal ion concentration was analyzed with AAS and adsorption capacity (q_e) at specified time (t) was calculated using equation no (1).

2.8.2 Biosorption thermodynamics study

The spontaneous biosorption of metal ion on JSP was represented as the reaction involving the biosorption of metal ion (M^{2+}) from the liquid phase to the solid phase with lone pair of electron (Ä). It is considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below:

$$\ddot{A} + M^{2+} \rightleftharpoons A\text{-}M$$

The distribution constant, Kc, used to evaluate the thermodynamic parameters was calculated using the following equation.

$$K_C = \frac{\mathrm{Cad}}{\mathrm{Ce}} \tag{3}$$

Where, Cad is mg of adsorbate adsorbed per liter; Ce is the equilibrium concentration of solution, mg/L

The Gibb's free energy change of the process can be calculated from the following equation which is related to equilibrium constant

$$\mathrm{Kc.}\ \Delta G° = -RT\ln K_c \tag{4}$$

Where, R is the universal gas constant (8.314×10^{-3} kj/mol/K) and T is the reaction temperature in Kelvin. A positive value of free energy (ΔG°) is indicated that the biosorption process is non-spontaneous in nature [13].

2.8.3. Evaluation of adsorption by isotherm modelling

Langmuir isotherm

Langmuir and Freundlich [14] isotherm models were studied for the evaluation of biosorption of Cr(III), Cd(II) and Pb(II) on JSP. The Langmuir isotherm is used for monolayer adsorption onto a surface containing a finite number of identical binding sites[14]. Following linear equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{5}$$

Where, Ce is the equilibrium concentration of adsorbate (mg L^{-1})
qe is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}).
q_m is maximum monolayer coverage capacity (mg g^{-1}),
K_L is Langmuir isotherm constant (l/mg) related to the affinity between the sorbent and the sorbate.

The constants q_m and K_L can be obtained from the slope and intercept of the plot of C_e/q_e against C_e.. 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 (6).

$$R_L = \frac{1}{1+K_L C_0} \tag{6}$$

According to Mckay *et al.*[15] 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.

Freundlich isotherm

Freundlich isotherm model is based on the assumption of heterogeneous surfaces as well as multilayer sorption and also being the binding sites are not equivalent. It can be rearranged to the following linear form (7):

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

Where, K_F is a constant describing the adsorption capacity (l/g) and n is an empirical parameter related to the adsorption intensity can be determined from the plot of $\log q_e$ against $\log C_e$. The constants *n* and K_F must be obtained from the slope and intercept, respectively. An important characteristic of the Freundlich isotherm is its ability to give an appropriate description of equilibrium data over a restricted range of concentration. According to Kadirvelu and Namasivayam [16] the value of *n* between 1 and 10 represents a beneficial adsorption process.

Temkin isotherm

Temkin isotherm contains a factor that explicitly takes into account the adsorbent–adsorbate interactions. The equation, its derivation is characterized by a uniform distribution of binding energies. By plotting the quantity sorbed q_e against lnCe the constants can be determined from the slope and intercept. The model is given by the following equations (8).

$$q_e = B\ln A_T + B\ln C_e \tag{8}$$

Where, A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R= universal gas constant (8.314 J/mol/K), T is Temperature at 298 K, B is Constant related to heat of sorption (J/mol).

Dubinin-Radushkevich (D-R) isotherm model

Another isotherm model applied in this study is Dubinin-Radushkevich isotherm model. The basic principle of this model is the Polany's adsorption potential theory and Dubinin's minipore filling theory can be given by the following equation [17].

D-R isotherm model can be rearranged to the following linear form of the equation (9):

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

Where, q_m and K_D are the constants of D-R isotherm model respectively, the maximum adsorption capacity (mol g^{-1}) and the adsorption energy. 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 biomass, E, which can be calculated using the following relation (10):

$$E = \frac{1}{(2K_D)^{\frac{1}{2}}} \tag{10}$$

The values of q_m and K_D may be obtained from the slope and the intercept of lnqe versus ε^2plot.

2.9. Determination of biosorption kinetics

One set of experiment was conducted under stirring condition (180 rpm) using aqueous solution of Cr(III), Cd(II), and Pb(II) ions with initial concentration of 50 mg L^{-1}. The amount of the JSP was maintained constant, equal to 0.5g in 100 mL solution in each of the batch experiments at different time intervals. Results generated from AAS were plotted as the contact time vs. the removal efficiency of Cr(III), Cd(II), and Pb(II) ions. The equilibrium time of contact required to remove Cr(III), Cd(II), and Pb(II) ions from the solution was 30-35 minutes. The results, obtained in the batch study, were used to investigate the kinetics of the Cr(III), Cd(II), and Pb(II) ions adsorption on the surface of JSP. Biosorption kinetics has been divided into two steps: a very rapid initial adsorption step followed by slow adsorption step [18]. 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. Tested kinetic models were; Lagergren's pseudo-first order, McKay and Ho's pseudo-second-order.

2.9.1. Pseudo –First Order Equation

The linear form (11) of the pseudo-first-order equation of Lagergren [19] is expressed as

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \tag{11}$$

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 constants were determined experimentally by plotting log (q_e-q_t) versus t. Both, adsorption reaction models and adsorption diffusion models are applied to describe the kinetic process of adsorption though they are quite different in nature [20]. At present, adsorption reaction models have been widely developed or employed to describe the adsorption kinetics [21]. To develop sorption kinetics, knowledge of the rate law describing the sorption system, is required.

2.9.2. Pseudo-Second-order equation

Based on the adsorption capacity at equilibrium, the pseudo-second-order equation can be expressed by following equation (12) [22].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

Where k_2 (g/mg min$-^1$) is the rate constant of the second-order equation. k_2 and q_e can be obtained from intercept and slope of the plot of t/q_t versus t. The pseudo-second-order rate constant k_2 and q_e were determined from the plot.

The pseudo-second-order rate expression was used to describe chemisorption involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate through covalent forces and ion exchange.

3. Results and discussion

There is no significant use of Jute stick in Bangladesh except for cooking purpose or fencing. Nowadays, Jute stick is also used in the production of charcoal. The spectroscopic study revealed that it has some functional groups which are very significant to bind heavy metal ions. Therefore, our target is to study the sorption performance of Jute stick powder as a potential adsorbent of heavy metal ions.

3.1. Characterization of biosorbent

Biosorbent is the lignocellulosic materials containing various functional groups which are the binding sites for the adsorption of heavy metal ions. Before and after loading Pb(II), Cr(III) and Cd(II) metal ions the Jute stick powder was investigated by FTIR and SEM method which revealed some vital information about the change of the data in two states.

3.2. FTIR spectroscopy analysis

FTIR spectra were taken for raw biosorbent and metal loaded biosorbent to reveal the systematic changes in the spectral positions. The preliminary qualitative analysis of major functional groups present in JSP (Jute Stick Powder) was obtained in FTIR spectra. The change of spectral pattern in stretching and bending of active groups due to adsorption of Pb(II), Cr(III) and Cd(II) ions on JSP was identified. It is assumed that for the O-H stretching vibrations a broad and intense adsorption peak was found at 3337 cm^{-1}. 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 1593 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 [23]. C-O stretching vibration of carboxylic acids and alcohol is found in the band range 1300-1000 cm^{-1}. Carboxyl and hydroxyl groups were present abundantly in the biopolymer JSP and these groups act as proton donors resulting deprotonated hydroxyl and carboxyl groups which may be involved in coordination with metal ions [24]. It was observed a board intense peak at the region 3337

cm^{-1} due to OH starching bond likely to become diminished for the Pb(II), Cr(III) and Cd(II) loaded JSP surface because –OH groups are bonded with metal ion. FTIR spectra of metal Pb(II), Cr(III) and Cd(II) sorbed Jute Stick Powder showed that the peaks expected at 2872, 1593 and 1055 cm^{-1} had shifted, respectively, 2842, 1592, and 1050 cm^{-1} due to Pb(II), Cr(III) and Cd(II) ions biosorption. These shifts might be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, were predominant contributors in metal ion uptake [25].

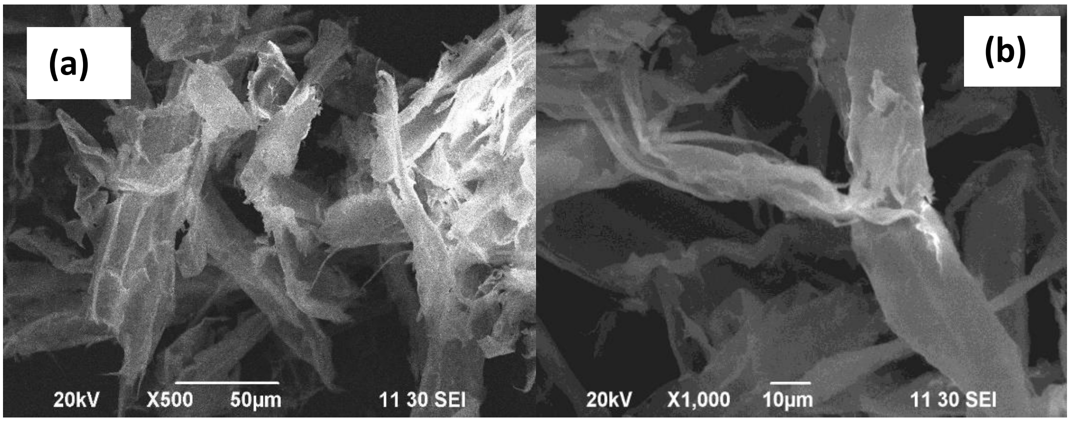
3.3. Scanning electron micrographs (SEM) analysis

Figure 1 represents the SEM micrograph which revealed some significant features of the surface structure. JSP without metal loaded and after metal loaded was taken for SEM analysis. The initial structure of the JSP is, as shown in figure 1(a). Figure 1(b) reveals the combination of small and large particles, heterogeneous rough and porous surfaces. Textured and porous surfaces were found on the JSP, which was expected to promote the uptake of metal ions. Figure 1(c) and Figure 1(d) represent the SEM micrograph of JSP after adsorption of Pb(II), Cr(III) and Cd(II) ions.

3.4. Optimization the biosorption process

3.4.1. Effect of pH

pH influences the ionization of functional groups at the surface of a sorbent and hydrogen ions. In this study, experiments for biosorption of Pb(II), Cr(III) and Cd(II) on to jute stick powder was carried out at varied pH from 2 to 8 (figure 2). At pH 2, it was observed that the adsorptions were poor. This was attributed to the active sites being widely protonated, which limited the adsorbing sites for the metal ions [26]. Figure 2 shows that the "% adsorption vs. pH" plots which revealed that the amount of Pb(II) adsorbed has increased from 37.4% to 98.64% by increasing the pH from 2 to 6 and reached a plateau at pH 6. For Cr(III), the amount of percent adsorption has increased from 60.1% to 96.2% by increasing the pH from 2 to 8. For Cd(II), the amount of percent adsorption has increased from 60.1% to 96.2% by increasing pH from 2 to 8. Above the value of pH 6 metal ions might be precipitated as hydroxides resulting the decreasing the adsorption.



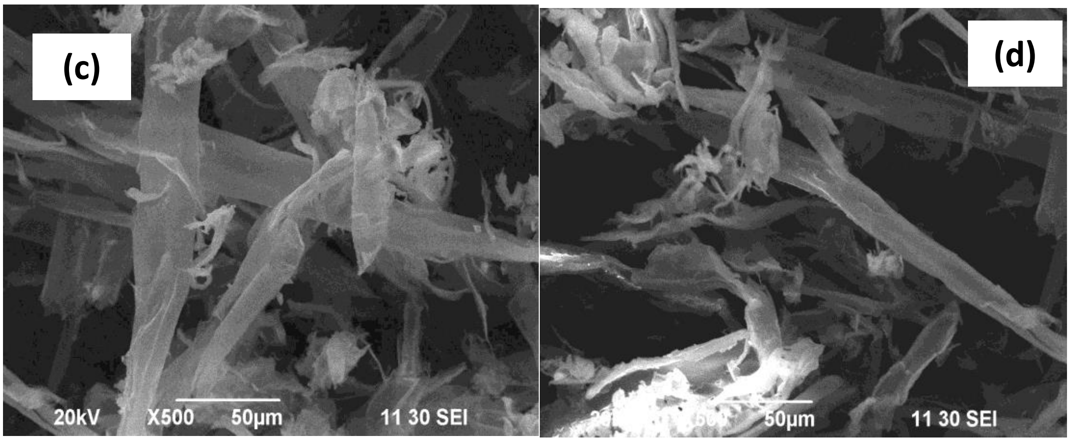


Fig. 1. SEM micrograph of JSP (a) (b) before and (c) (d) after adsorption of Pb(II), Cr(III) and Cd(II) ions as multi-components.

3.4.2. Effect of contact time

The effect of contact time on the adsorptive removal of Pb(II), Cr(III) and Cd(II) at 28^{0}C is shown in figure 3, which reveals that the rate of sorption of lead, chromium and cadmium on Jute Stick Powder was rapid, with 60-70% of adsorption occurring within the first 30 min and attained equilibrium at 40 min and the percent uptake of metal ions increased rapidly to 97.3% for Pb(II), 99.2% for Cr(III) and 81.6% for Cd(II).This behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the sorbent followed by an internal diffusion process, which may be the rate determining step. The adsorption process 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 was observed that with further increase of time, there was no significant increase of biosorption of these metals. This is because there was saturation of the active sites on the biomass and leading to a repulsive force between the adsorbate and adsorbent [27].

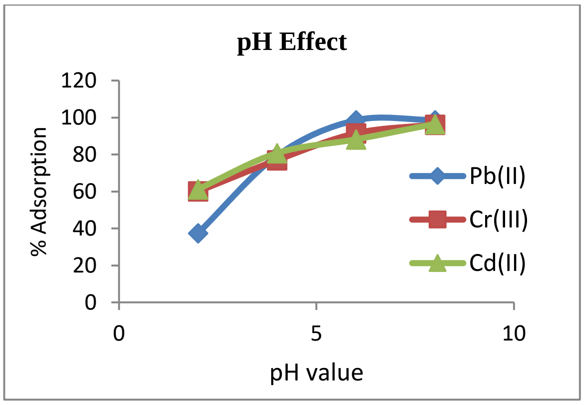


Fig. 2. Effect of pH on percent adsorption of Pb(II), Cr(III) and Cd(II) from water by JSP

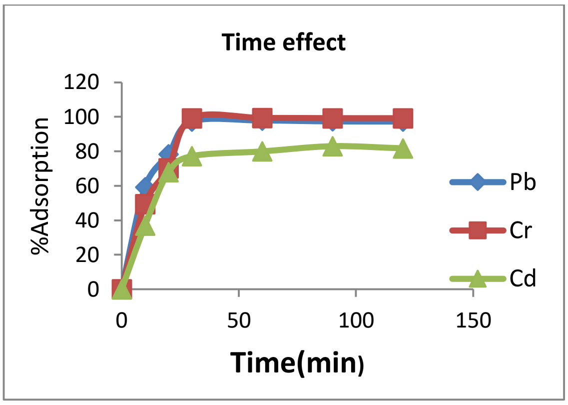


Fig. 3. Effect of time on percent adsorption of Pb(II), Cr(III) and Cd(II) from water by JSP.

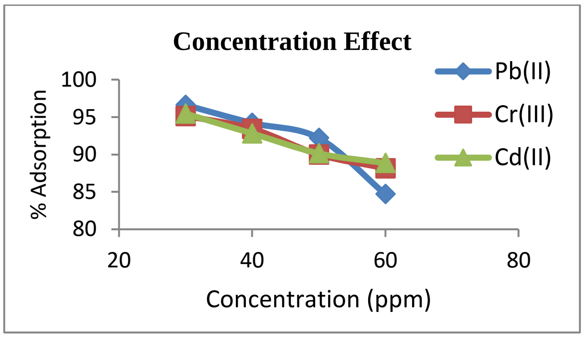


Fig. 4. Effect of initial concentration on percent adsorption of Pb(II), Cr(III) and Cd(II) from water by JSP

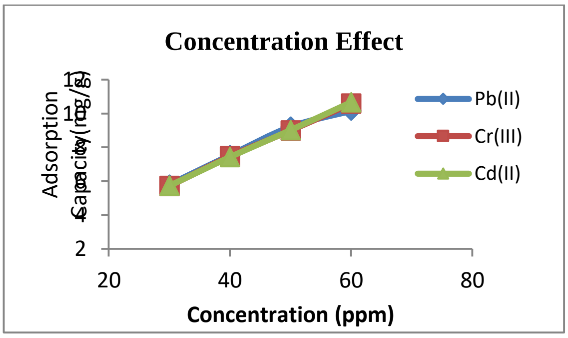


Fig. 5. Adsorption capacity of JSP on different concentration of Pb(II), Cr(III) and Cd(II) from water

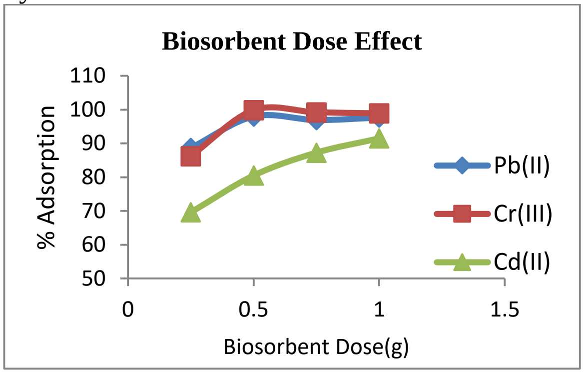


Fig. 6. Effect of biosorbent dose on percent adsorption of Pb(II), Cr(III) and Cd(II) from aqueous solution by JSP

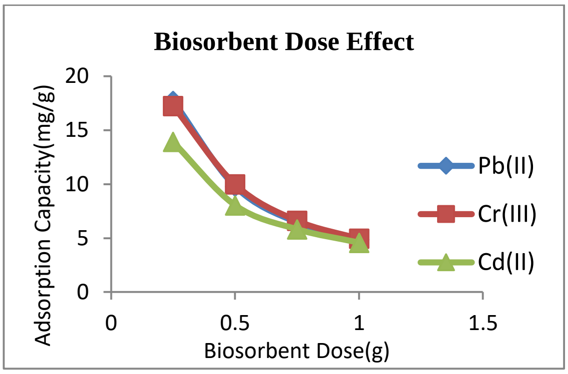


Fig. 7. Adsorption capacity of JSP on different biosorbent dose from aqueous solution of Pb(II), Cr(III) and Cd(II)

3.4.3. Effect of initial metal ion concentration

Initial metal ion concentration strongly affects the extent of removal of heavy metals from aqueous solution. In order to assess this, sorption experiments were performed at the initial metal ion concentration of 30, 40, 50 and 60 mg L^{-1} at pH 6.0 with 0.5 g of biosorbent added into 100 ml solutions at 28ºC. According to figure 4, the results demonstrate that at a fixed adsorbent dose, the percentage of adsorption decreased with increasing concentration of solution. At higher concentrations more Pb(II), Cr(III) and Cd(II) ions were left unadsorbed in solution due to the saturation of binding sites at a fixed dose(0.5g). The figure discloses that the removal of Pb(II),Cr(III), Cd(II) by Jute stick powder decreased from 96.63% to 84.7%, 95.13% to 88.15% and 95.46% to 88.86%, respectively when the concentration increased from 30 ppm to 60 ppm. On the contrary, adsorption capacity for each gram adsorbent increased gradually from about 5.7 mg/g to 10.6 mg g^{-1} with the increase of concentration (shown in figure 5). This result can be explained that at lower concentrations, the ratio of number of metal ions to the available sorption sites was low and subsequently the fractional adsorption became independent of initial concentration. Hence, the removal of metal in depended on the initial metal ions concentrations and decreased with an increase in initial metal ions concentration [28].

3.4.5. Effect of adsorbent dosage

The amount of adsorbent is key factor as the adsorption mainly depends upon the surface area of adsorbent available for the contact of metal ions. To study the effect of biosorbent dosage on the removal of Pb(II), Cr(III) and Cd(II) the biosorbent dosage was changed from 0.25g to 1.0g keeping other parameters (pH, initial concentration and temperature) constant. The results were graphically represented in figure 6. For Pb(II) and Cr(III) the maximum removal (97.96%) was attained with the dose of 0.5g. But Cd(II) showed gradually increase with the increase of biosorbent dosage and reached maximum at the dose of 1g. Further increase in the biosorption dosage did not significantly change the biosorption percentage. Hence the amount of ions bound to the adsorbent and the amount of free ions remained constant even with further addition of the adsorbent dosage. The percentage removal of Pb(II), Cr(III) and Cd(II) increased with an increase in adsorbent dosage. It is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. On the other hand, uptake capacity or amount of metal adsorbed (q, mg g^{-1}) decreased with an increase in biosorbent dose from 0.25-1.0 g L^{-1} (figure 7). This might be because with increased biomass, there would be an increased amount of unsaturated active sites [29]. After a certain dose, the amount of adsorption may decrease due to the particle interactions such as aggregation leading to a decrease in the total surface area of the sorbent [30].

3.5. Adsorption isotherm

The adsorption isotherm indicates how the adsorbate distributes between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state at a constant temperature. The adsorption data were analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models.

3.5.1. Langmuir isotherm model

The Langmuir isotherm is derived from the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with constant energy of adsorption, and no transmigration of adsorbate in the plane of the surface. This isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between adsorbed species is expressed by the mathematical relation (Eq. 5). Figure 8 (a-c) is a plot of linear form of the isotherm (eq. 6) which shows the experimental data presented as 1/Cevs 1/qe. By calculating the slope and intercept Langmuir isotherm parameters were determined. The values listed in the table 1 give significant information about the adsorption process. The maximum adsorption capacities of Jute stick powder calculated from Langmuir isotherm is 11.11 mg g^{-1} for Pb(II), 12.71 mg g^{-1} for Cr(III),12.22 mg g^{-1} for Cd(II). These are greater than the corresponding experimental values 10.164 mg g^{-1} for Pb(II), 10.578 mg g^{-1} for Cr(III) and 10.664 mg g^{-1} for Cd(II). The values of R_L ranged from 0.015 to 0.030 for Pb(II), 0.029 to 0.057 for Cr(III) and 0.026 to 0.050 for Cd(II) ions, respectively in the initial metal ion concentrations 30-60 mg L^{-1}. The values of R_L indicated that the adsorption process is favorable because it is within the range $0<R_L<1$. The isotherm curves are fit well with the experimental data showing the regression R^2 = 0.965-0.990 for all ions. The low value of K_L (0.55-1.06) obtained from the Langmuir isotherm indicated that Jute Stick powder has a high affinity for metal ions which correlated with the interpretation by several authors [31].

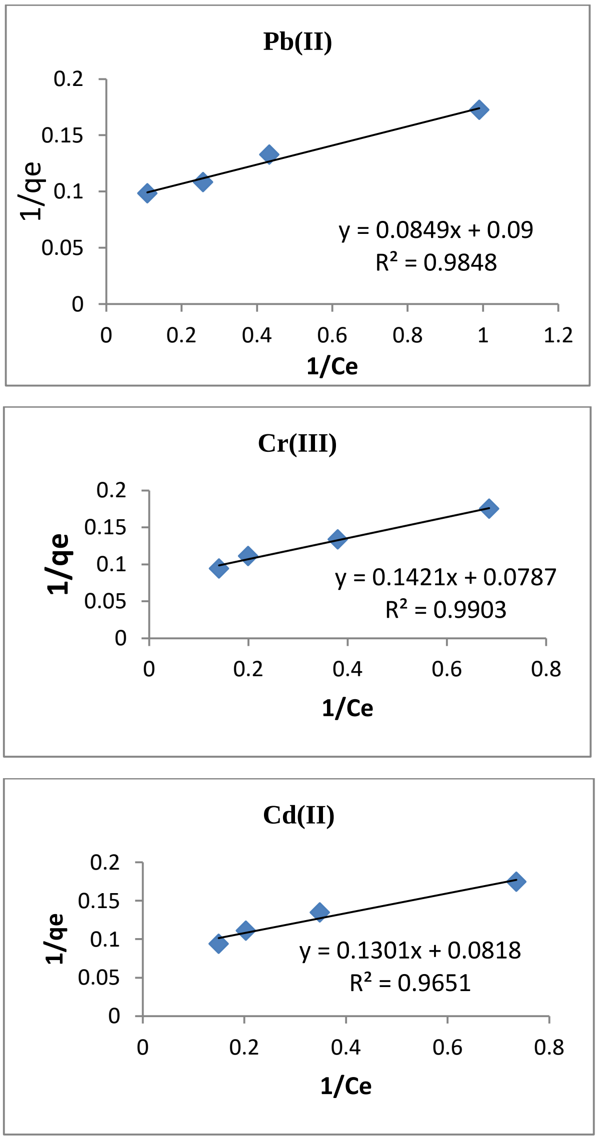


Fig. 8 (a-c). Langmuir isotherm for adsorption of Pb, Cr, Cd on Jute stick powder (Temp: 28°C, dosage : 0.5 gm, time: 60 min, pH= 6)

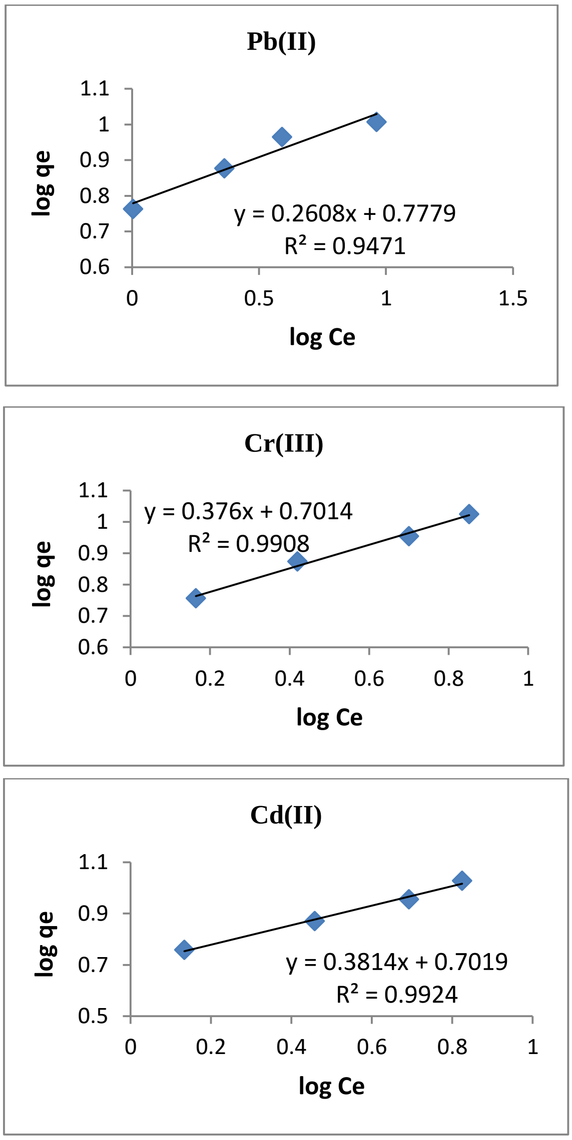


Fig. 9 (a-c). Freundlich isotherm for adsorption of Pb, Cr, Cd on jute stick powder. Reaction condition: (pH 6, time 60 min, temp 301K, doses 0.5g, speed 180rpm)

3.5.2. Freundlich isotherm

Freundlich isotherm gives the relationship between the equilibrium liquid and solid phase capacity based on multilayer adsorption (heterogeneous surface). The linear form of the Freundlich isotherm equation is expressed by equation 7 and figures 9 (a-c) shows a plot of log q_e against log C_e. Value Freundlich isotherm constant *n* is an empirical parameter related to the adsorption intensity and K_F is a constant describing the adsorption capacity (L g^{-1}). Kadirvelu and Namasivayam [16] reported that the value of *n* between 1 and 10 represents a beneficial adsorption process. The values of n and K_F are calculated from the slope and intersect of the curve which are found 3.831 and 5.998 for Pb(II),2.625 and 5.023 for Cr(III) and 2.625 and 5.035 for Cd(II), respectively as presented in the table 1. The value of *n* obtained lies within range 1 to 10 implies that Jute stick powder has a high affinity for metal ions in solution. Regression coefficient of curve was 0.992 indicating that this isotherm gave a good and better fit to the experimental data. Therefore, The Freundlich isotherm was the best fit for lead biosorption using Jute stick powder in the present study which is in close agreement with the result shown by many authors discussed in literature [32].

3.5.3. Temkin adsorption isotherm

Temkin isotherm model predicts the effects of indirect adsorbate-adsorbent interactions on the adsorption process. It is believed that with the increase of the surface coverage the heat of adsorption (ΔH_{ads}) of metal ions in the layer decreases linearly [33]. Equation (8) obtained from linear form of Temkin isotherm model is plotted as qe vs lnCe as shown in figure 10 (a-c). Two constants, A_T and B_T are calculated from the slope and intercept of the curve found 18.185 and 1213.31 for Pb(II), 4.682 and 8.387for Cr(III) and 4.640 and 829.45, respectively and the regression coefficient (R^2) was found better than 0.965 which is an indication of the heat of sorption indicating a physical adsorption (table 1). According to the value of Temkin isotherm constants, Temkin isotherm model could be used to evaluate the adsorption confirmation of Cd(II) ion onto Jute stick powder biosorbent. The binding energy of the adorbate and adsorbent was higher than 2.954 J/mole for all ions.

3.5.4. Dubinin-Radushkevich Isotherm

Dubinin-Radushkevich (D-R) model in which assumption is not based on homogenous surface or constant adsorption potential, and gives insight into the biomass porosity as well as the adsorption energy. From the values of adsorption energy the chemical or physical nature of adsorption process could be known. The mathematical expression of D-R model is explained by equations (9, 10). q_m and K_D are the constants of D-R isotherm model represent the maximum adsorption capacity (mol g^{-1}) and the adsorption energy respectively. The constant K_D is related to the mean free energy of sorption per mole of the adsorbent which is termed as E (kJ/mol). The figure 11 (a-c) represented the plot of equation 9 where $q_m$vs ε^2. The constants q_m and K_D are calculated from the curve found 0.819 and $2E^{-07}$ for Pb(II), 0.837 and $4E^{-07}$ for Cr(III), 0.829 and $3E^{-07}$ for Cd(II), respectively. If the value of the mean free energy of adsorption per molecule of the adsorbate when transferred to the surface of the solid from infinity in solution (E) lies between 8 and 16kJ mol^{-1} the sorption process is a chemisorption one, while values of below 8kJ mol^{-1} indicates a physical adsorption process [34]. From the plot, regression constant R^2 are found 0.869-0.918 indicating that these isotherms provided a good fit to the experimental data.

3.6. Adsorption kinetic based models

Biosorption kinetics depends on the interactions of between adsorbate and adsorbent. The potential rate controlling steps of biosorption of Pb(II) ions onto the jute stick powder system which include mass transport and physical-chemical interactions have been investigated using adsorption reaction based models. To observe the biosorption behavior the experimental data were exploited into two kinetic equations such as pseudo-first order and pseudo-second order kinetic models.

3.6.1. Pseudo- first order reaction model

The first rate equation for sorption in a liquid/solid system based on solid capacity was the Lagergren rate equation 11. This equation can be linearized for use in the kinetic analysis of experimental results [35]. The first-degree kinetic model is obtained by linear drawing of log (qe-qt) on the basis of t, which k_1 and qe are drawn from slope and intercept, and R^2 correlation coefficient can be also obtained from the diagram. The pseudo first order rate constant can be obtained from the slope of plot in figure 12 (a-c) that shows the pseudo-first order kinetic plot for the biosorption of metal ions onto Jute stick powder. The pseudo first order rate constant values were calculated from the slope and intercept of plot.

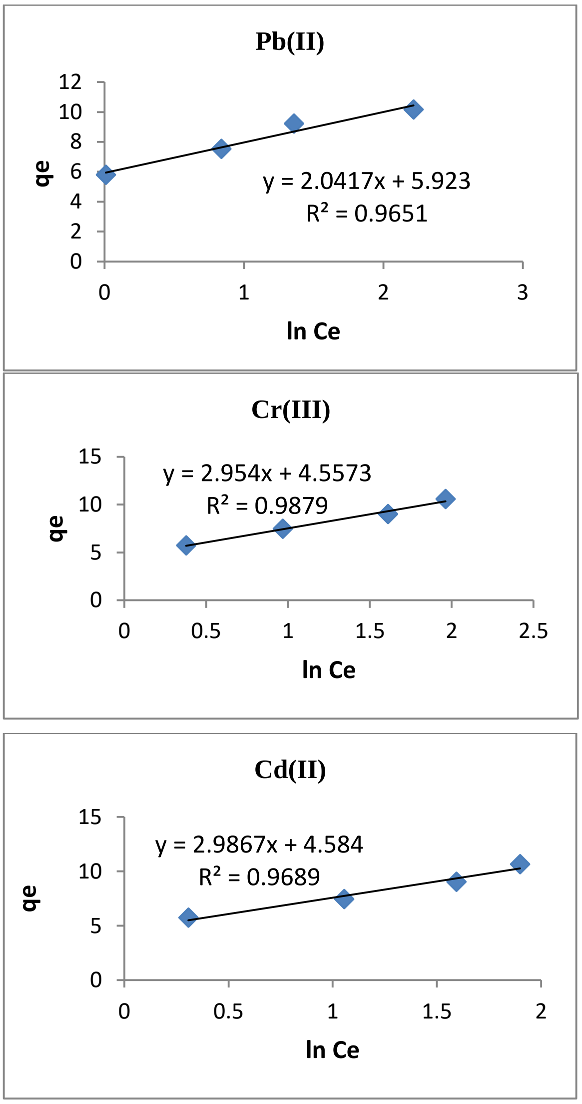


Fig. 10 a-c. Temkin isotherm for adsorption of Pb, Cr, Cd on jute stick powder. Reaction condition: (pH 6.0, time 60 min, temp 301K, doses 0.5g, speed 180rpm)

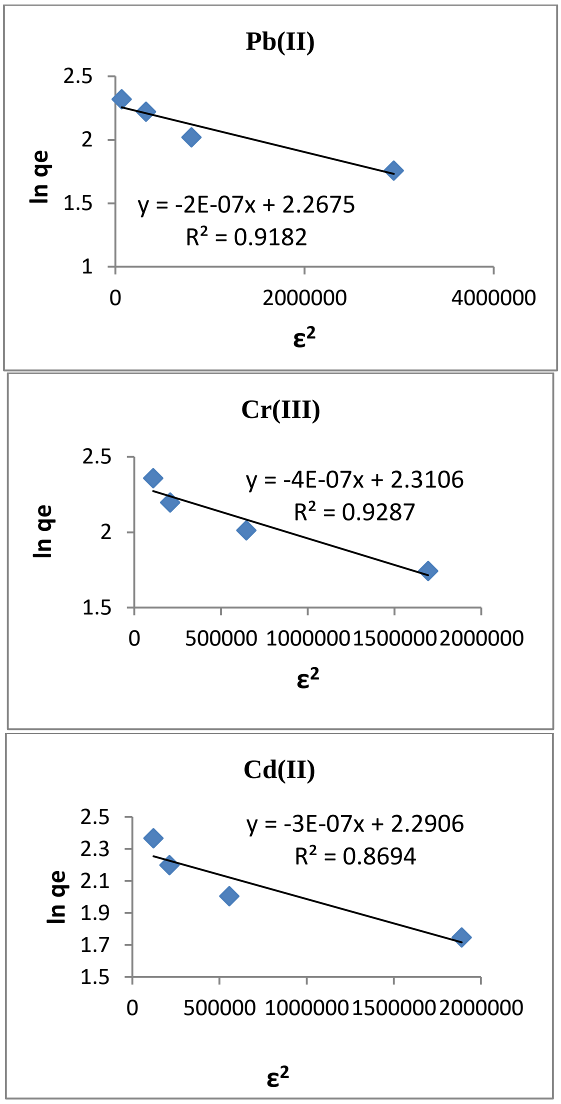


Fig. 11 a-c. Dubinin-Radushkevich isotherm model on the adsorption of Pb, Cr, Cd by jute stick powder (pH 6.0, time 60 min, temp 301K)

The calculated values and their corresponding linear regression correlation coefficient values are shown in table 2**.** It was observed that the calculated value of maximum adsorption capacity was 6.776 mg g^{-1} for Pb(II), 4.335 mg g^{-1} for Cr(III) and 5.284 mg g^{-1} for Cd(II) which was nearly concordance with the corresponding experimental value of maximum adsorption capacity 9.73 mg g^{-1}, 8.05 mg g^{-1} and 8.18 mg g^{-1}. Therefore it can be considered that the adsorption system follows pseudo second order kinetics. The pseudo first order rate constant values were found 0.052-0.059 min^{-1} and the correlation coefficient value were found to be 0.959-0.997, which shows that this model can be applied to predict the adsorption kinetic model.

Table 1. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherm parameters for adsorption of Pb(II), Cr(III) and Cd(II) by jute stick powder

Langmuir isotherm constant

Metal ion	**q_{max} (mg g^{-1}) (exp.)**	**q_{max} (mg g^{-1}) (cal.)**	**K_L (mg g^{-1})**	**R_L**	**R^2**
Pb(II)	10.164	11.11	1.06	(0.015-0.030)	0.985
Cr(III)	10.578	12.71	0.55	(0.029-0.057)	0.990
Cd(II)	10.664	12.22	0.63	(0.026-0.050)	0.965

Freundlich isotherm constant

Metal ion	**1/n**	**n**	**K_F**	**R^2**
Pb(II)	0.261	3.831	5.998	0.947
Cr(III)	0.376	2.660	5.023	0.991
Cd(II)	0.381	2.625	5.035	0.992

Temkin isotherm parameter

Metal ion	**B** (J mol^{-1})	**B_T**	**A_T** (L/g)	**R^2**
Pb(II)	2.042	1213.31	18.185	0.965
Cr(III)	2.954	838.72	4.682	0.988
Cd(II)	2.987	829.45	4.640	0.969

Dubinin-Radushkevich isotherm constant

Metal ion	**q_m (mol g^{-1})**	**K_D (mol^2/J^2)**	**E (J/mol)**	**R^2**
Pb(II)	0.819	$2E^{-07}$	1581	0.918
Cr(III)	0.837	$4E^{-07}$	1118	0.929
Cd(II)	0.829	$3E^{-07}$	1291	0.869

3.6.2. Pseudo-second order reaction model

This model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step [36]. The plot of t/qt Versus t, for pseudo-second order model applied to the biosorption of Pb(II), Cr(III) and Cd(II) by Jute stick powder is shown in figure 13 (a-c). The k_2 and q_e calculated and correlation coefficient Pb(II), Cr(III) and Cd(II) are given in table 2**.** From the isotherm model, the results revealed that the maximum adsorption capacity are 7.03 mg g^{-1} for Pb(II), 6.78 mg g^{-1} for Cr(III) and 6.23 mg g^{-1} for Cd(II) which are lower than the corresponding experimental value 9.73, 8.05 and 8.18 mg g^{-1}. The values of K_2 are 0.0389 min^{-1}, 0.0497 $min^{-1}$and 0.0356 min^{-1} for Pb(II), Cr(III) and Cd(II), respectively. The regression coefficients were found 0.870-0.915 indicating that experimental data were fitted well with the Pseudo- second order equation for all metal ions. Therefore, their biosorption onto Jute stick powder can be described by both pseudo-first order and pseudo-second order equation for Pb(II), Cr(III).But biosorption of Cd(II) onto Jute stick powder can be described by pseudo- first order only.

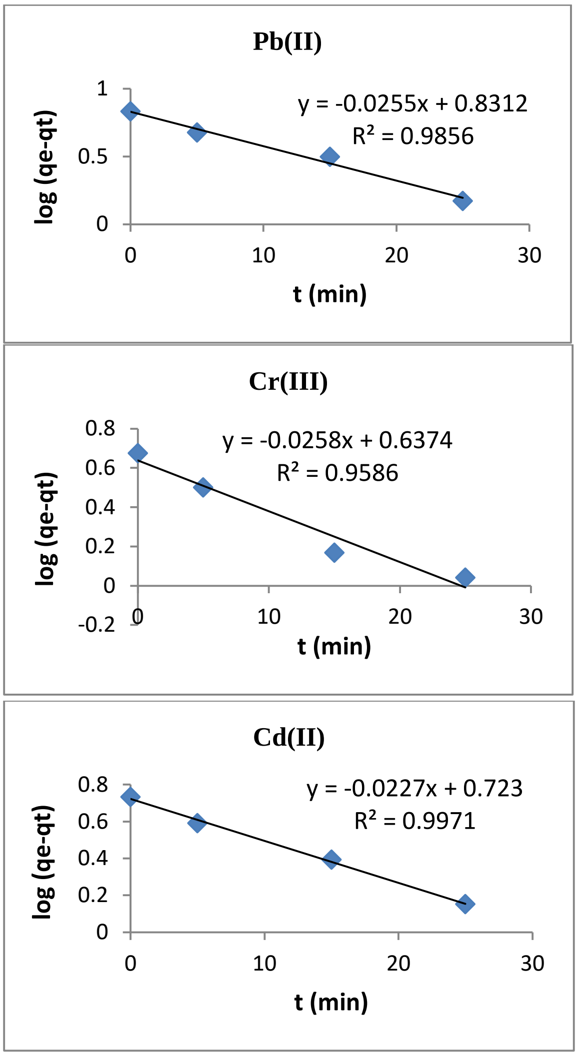


Fig. 12 a-c. Pseudo-1st order model on the adsorption of Pb, Cr, Cd by jute stick powder

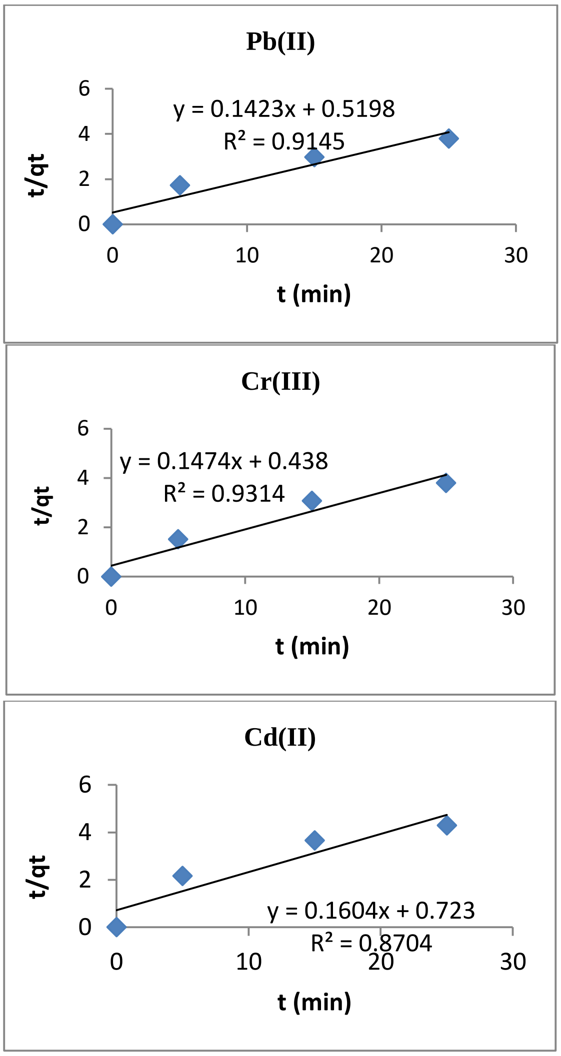


Fig. 13 a-c. Pseudo-2nd order model on the adsorption of Pb, Cr, Cd by jute stick powder

Table 2. Pseudo-1st order and Pseudo-2nd order model parameter for adsorption of Pb(II) by jute stick powder

Pseudo-1st order model parameter				
Metal ion	**q_e, exp (mg g^{-1})**	**q_e, cal. (mg g^{-1})**	**K_1(min^{-1})**	**R^2**
Pb(II)	9.73	6.776	0.059	0.986
Cr(III)	8.05	4.335	0.059	0.959
Cd(II)	8.18	5.284	0.052	0.997
Pseodo-2nd order kinetics parameter				
Metal ion	**q_e, exp (mg g^{-1})**	**q_e, cal. (mg g^{-1})**	**K_2 (min^{-1})**	**R^2**
Pb(II)	9.73	7.03	0.0389	0.915
Cr(III)	8.05	6.78	0.0497	0.931
Cd(II)	8.18	6.23	0.0356	0.870

3.6.3 Desorption and regeneration studies

Figure 14 shows the percentage of desorption of metal ions from biosorbent using different reagent. The highest desorption of Pb(II), Cr(III) and Cd(II) from the metal loaded JSP by 0.1M HCl resulted in 76.44% and by distilled water as a lowest amount metal recovery 22.77% for first cycle. For the reuse and regeneration of the biosorbent five times was carried out using 0.1M HCl and found first three times remained almost unchanged and then gradually reduced for the fourth and fifth cycles. It was observed that 0.1M NaOH and distilled water desorbed Cd(II) ions in very little amount. Desorption of metal ions with acidic solution is greater indicates that adsorption is in low pH is less and metal ions are exchanged by hydrogen ion. Similar results were also reported by several researchers using different agro-based biosorbents [37].

3.7. Industrial waste water treatment by biosorbent

Industrial waste water can be purified by removing toxic heavy metals which can pose serious health risks. After collecting industrial waste water, it was treated with jute stick powder (JSP) and heavy metals were removedfrom it. Removal of lead, chromium and cadmium from industrial waste water is discussed here.

3.7.1 Removal of Pb(II), Cr(III) and Cd(II) from wastewater

It was observed that (Figure 15a) initially industrial wastewater contained 3.68, 11.66, 1.02 and 7.24 ppm Pb(II) ions, respectively. But after treatment of industrial wastewater through biosorption process, the final metal ion concentration was reduced. It was found that the final concentration of Pb(II) ions was 1.66, 9.52, 0.38 and 3.02 ppm, respectively. Thus Pb(II) ions can be removed through biosorption process. The initial concentration of Cr(III) ions (figure 15b) in industrial wastewater was 5.52, 2.44, 0.78 and 0.76 ppm Cr(III) ions, respectively. But after treatment of industrial wastewater through biosorption process, the final metal ion concentration was reduced. It was found that the final concentration of Cr(III) ions was 1.64, 0.86, 0.42 and 0.34 ppm, respectively. The initial concentration of Cd(II) ions (figure 16c) in industrial wastewater were 10.68, 4.52, 0.88 and 0.58 ppm Cr(III) ions, respectively. But after treatment of industrial wastewater through biosorption processes, the final metal ion concentration was found to be 4.68, 2.76, 0.16 and 0.34 ppm, respectively.

3.7.2. Percentage of removal of metal ions and adsorption capacity JSP

It was observed that (Figure 16) the percentage of removal of Pb(II), Cr(III) and Cd(II) from industrial sample no. 1 was 54.89%, 70.29% and 56.18%, respectively. The percentage of removal of Pb(II), Cr(III) and Cd(II) from industrial sample no. 2 was 18.35%, 64.75% and 38.94%, respectively. The percentage of removal of Pb(II), Cr(III) and Cd(II) from industrial sample no. 3 was 62.75%, 46.15% and 81.82%, respectively. The percentage of removal of Pb(II), Cr(III) and Cd(II) from industrial sample no. 4 was found to be 58.29%, 55.26% and 41.38%, respectively. The adsorption capacity of jute stick powder (JSP) as biosorbent (figure 17) for the removal of Pb(II) from industrial wastewater samples was found 0.404, 0.428, 0.128 and 0.844 mg g^{-1}, respectively. The adsorption capacity for the removal of Cr(III) by biosorbent was found to be 0.776, 0.316, 0.072 and 0.084 mg g^{-1}, respectively. The adsorption capacity of jute stick powder (JSP) for the removal of Cd(II) was found to be 1.2, 0.352, 0.144 and 0.048 mg g^{-1}, respectively.

4. Conclusion

Biosorption of Pb(II), Cr(III) and Cd(II) by Jute sick powder biomass was found to be influenced by the solution pH, biosorbent dose, contact time, temperature and initial metal ion concentration. The kinetic studies indicated that the biosorption process followed pseudo-first-order, pseudo-second-order but the pseudo-first-order kinetics was better. Equilibrium studies showed that the biosorption of Cd(II) ions was well represented by both Freundlich and Langmuir isotherms but the Freundlich model gave a better fit. The biosorbent Jute stick powder could be regenerated and reused successfully for more than three times.

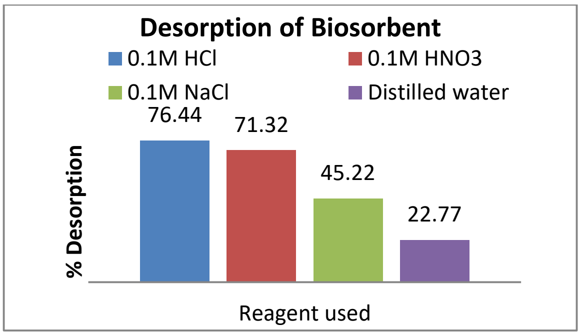


Fig. 14. Percent of desorption of metal ions from biosorbent using different reagent

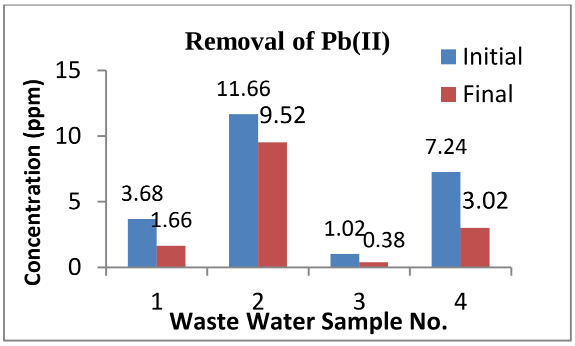


Fig. 15 a. Concentration of Pb(II), Cr(III), Cd(II) ion in waste water before and after biosorption process

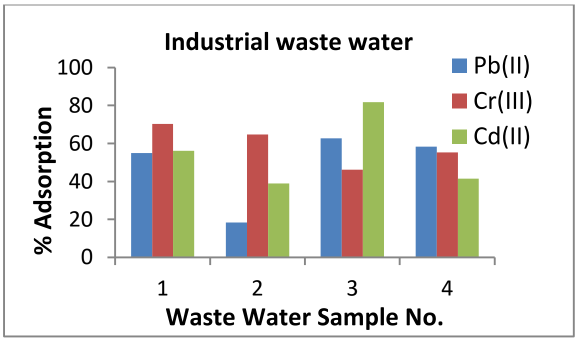


Fig. 16. Percent adsorption of Pb(II), Cr(III) and Cd(II) from industrial waste water by JSP

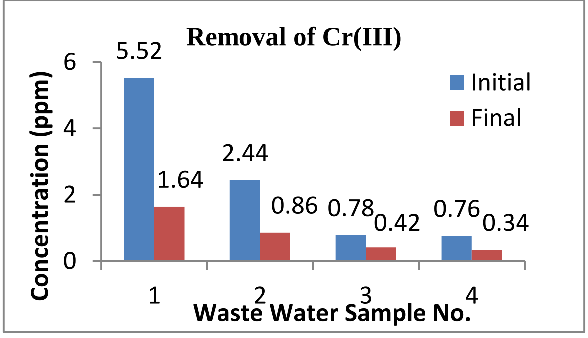


Fig. 15 b. Concentration of Pb(II), Cr(III), Cd(II) ion in waste water before and after biosorption process

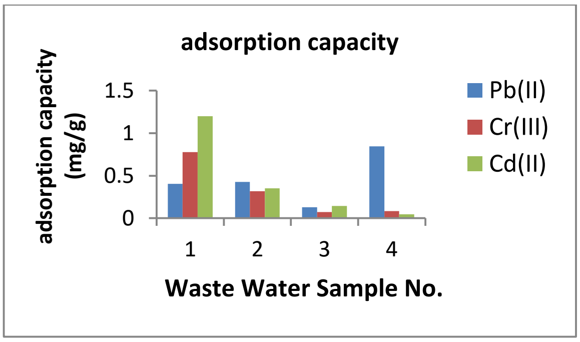


Fig. 17. Adsorption capacity of JSP as biosorbent for removal of Pb(II), Cr(III) and Cd(II) from industrial waste water.

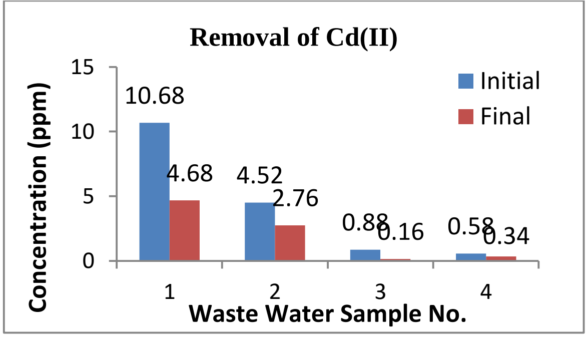


Fig. 15 c. Concentration of Pb(II), Cr(III), Cd(II) ion in waste water before and after biosorption process

The values of the thermodynamic parameters showed the spontaneous, endothermic and highly disordered nature of the biosorption of Pb(II), Cr(III) and Cd(II) from aqueous solution. The percentage of adsorption of Pb(II), Cr(III) and Cd(II) ions was found to decrease with the increasing concentration and increasing biosorbent dose. After a few minutes, the percentage of adsorption decreased with time. Biomass regeneration efficiencies up to 98% were achieved using an acid as eluent.

Acknowledgements

This study was partially funded by Research and publication cell, University of Chittagong, Bangladesh. Ref. 3665 (Res & pub. Cell. CU)/2019.

Conflict of Interest: The authors declare that they have no conflict of interest.

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