

Research Article

Biosorption Studies of Cd^{2+} and Cr^{6+} from Aqueous Solution Using Cola-Nut Leaves as Low-Cost Biosorbent

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Cola-nut leaf is an agricultural waste which was used in this research as biosorbent for the adsorption of Cd^{2+} and Cr^{6+} from aqueous solutions. The leaves of cola nut were modified using 0.1 M HCl. Modified cola nut leaves biosorbent showed slightly higher percentage sorption than the unmodified leaves, for both heavy metals with increasing contact time, having greater affinity for Cd^{2+} . The equilibrium sorption data was attained using the batch technique with increased pH (9) and increased adsorbent dose ($1 \text{ g}/25 \text{ cm}^3$ of adsorbate) and initial metal concentration. The functional group of cola nut leaves before and after adsorption was determined using Fourier Transform Infrared Spectroscopy (FTIR). Kinetics data were best fitted to a pseudo-second-order model. Equilibrium data were better described by the Temkin isotherm model with a multilayer adsorption capacity. The study showed that leaves of cola nut are a promising biosorbent for Cd^{2+} and Cr^{6+} which could be utilized for industrial wastewater remediation.

1. Introduction

Heavy metals are naturally occurring contaminants found in the environment as a result of their non-bio-degradability. The toxicity of heavy metals in air, soil, and water is a global issue because it poses threat to human, animal, and plant life. Anthropogenic activity has led to increase in the amount of heavy metals in the environment. Such activities include electroplating and metal treatment processes, printed circuit board (PCB) manufacturing, wood treatment processes, inorganic dye manufacturing, and petroleum refining [1]. Also, research has indicated that cleaning of process tanks and treatment of wastewater may produce reasonable amount of wet sludge having high levels of toxic metals [2].

The following are processes that were used in the removal of heavy metals from the aqueous solution: conventional chemical processes, which include processes such as chemical precipitation, flotation, ion exchange, electrochemical deposition, electro dialysis, electrolytic extraction, reverse osmosis, and cementation [3]. These methods are expensive and cannot remove metals at low concentration

[4]. Owing to low cost and availability of biomass, biosorption has received considerable attention in recent years.

Various plant leaves have been used as adsorbents for the removal of heavy metal ions from a solution [5, 6] and [7]. The search for readily available and more efficient biosorbents for removal of heavy metals from aqueous solution has led to the identification of cola nut leaves, which are evergreen plants, for this purpose.

Treatment of biomass for adsorption helps to desorb inorganic and organic materials adsorbed during plant growth which may affect the adsorption process [8] and also increases the capacity of the sorbent by cleaning up the surface and opening up pores [9]. The best chemical to treat the biomass involves the use of alkalis and inorganic or organic acids [8].

Although there are a number of reviews on the adsorption capacity of various biomasses which deal with elimination of heavy metals, however, considering the complexity of various factors that influence the process, highly-efficient biosorbents that are cost-effective need to be identified. According to Alekseeva et al. [10] in a review, the

biosorbents with greatest performance for removal of metal ions in the literature is sorption using leaves of neem tree which is an evergreen plant. Hence, the leaves of other evergreen crops (which are available all throughout the year) will be tested for their adsorption capacity. Hence, in this research, biosorption characteristics (pH, biomass dosage, initial metal concentration, and contact time) were studied for the adsorption of Cd^{2+} and Cr^{6+} onto dried cola nut leaves and acid-modified cola nut leaves.

2. Materials and Methods

2.1. Materials

2.1.1. Equipment. Buck Scientific Atomic Adsorption Spectrophotometer (AAS)-AAS-HP Serial Number: MY14470001, Agilent Technologies FTIR Spectrometer Happ-Ganzel Resolution 8, Stuart Scientific orbital shaker-SO1, JENWAY Digital pH meter, digital electronic balance, hot air oven (MINO/53/CLAD), Miller, rotary evaporator, Erlenmeyer flasks and volumetric flasks, Whatman filter paper, sieve, deionized water, beakers, measuring cylinder, stoppers, and masking tape.

2.2. Chemicals and Reagents. All reagents used are of analytical grade.

Cadmium (II) nitrate tetra-hydrate (percentage purity 99%, MW 308.47 g/mol), potassium dichromate hexa-hydrate (percentage purity 99%, MW 294.2 g/mol), NaOH (percentage purity 99%, MW 40 g/mol), and HCl (percentage purity 36.5%, specific gravity 1.18125).

2.3. Sampling. A composite sample of cola nut leaves was collected made up of leaves obtained from many trees from plantation in Ondo west local government, Ondo state. The leaves were stored in air-tight sacs. It was transported immediately and taken for identification, where a voucher number of 9171 was given to the plant.

2.4. Preparation of Leaves for FTIR Analysis. The dried powdered leaves of cola nut were weighed (10 g) and mixed with 150 ml of ethanol and kept for 3 days as described by Kumar and Ramaswamy [11]. The extract was filtered using Whatman no. 1 filter paper, and the filtrate was collected. It was evaporated using a rotary evaporator, and the crude was taken for Fourier Transform Infrared Spectrophotometry (FTIR) analysis. It is a tool that can be used to identify the types of chemical bonds in a compound and also the functional groups present in the compound.

2.4.1. Preparation of Cola Nut Leaves. Sample (cola nut leaves) was pretreated according to the method described by Tichaona and Olindah [8]; the plant leaves were washed with tap water and rinsed with distilled water to remove dirt and extraneous materials. It was sun-dried, then pulverized to a fine powder using a miller, sieved to obtain uniform particle size, and oven-dried at $105^\circ\text{C} \pm 0.1$ to constant mass. Finally,

it was stored in a plastic container. The functional groups in cola nut leaves were determined using the Agilent Technologies FTIR Spectrometer, Serial Number: MY14470001 model 8.

2.4.2. Modification of the Sample. The acid modification was carried out as described by Ege and Doner [12]. Exactly 10 g of the powdered sample was mixed with 200 cm^3 of 0.1 M HCl solutions for 72 hours at room temperature and then rinsed with distilled water until a pH of 7 was obtained. It was dried in an oven for three days at 60°C and kept in plastic containers, (labeled ATK) for adsorption processes. A control, untreated cola (UTK), was also used as biosorbent for the adsorption of Cd and Cr ions.

2.4.3. Preparation of the Adsorbate. Stock solutions of Cd^{2+} and Cr^{6+} metal ions were prepared using the standard method, from which working concentrations (5, 50, 100, 150, and 200) mg/L were prepared by serial dilution.

2.5. Batch Biosorption Procedure. For acid-modified cola nut leaves (ATK) and unmodified (UTK) samples, batch experiments were carried out. The powdered sample (0.1 g) was mixed separately with 25 cm^3 metal ion solution of initial concentration 100 mg/L. The mixture was shaken constantly on a shaker at 200 revolutions per minute (rpm) at given time intervals, at the end of which the mixture was filtered using a filter paper, and the filtrate was taken for analysis, as described by Tijani et al. [13]. Residual concentration was immediately determined using an atomic absorption spectrophotometer AAS. This was carried out in triplicate, and the mean value was taken. The removal efficiency (% sorption) and adsorption capacity were calculated using equations (1) and (2), respectively, as described by Dada et al. [14]:

$$\% \text{ sorption} = \left(\frac{C_o - C_e}{C_o} \right) \times 100, \quad (1)$$

$$Q_e = \frac{C_o - C_e}{m} V, \quad (2)$$

where C_o is the initial metal ion concentration in mg/L, C_e is the equilibrium metal ion concentration in mg/L, m is the amount of adsorbent in g, and V is the amount of adsorbate in cm^3 .

Effect of operational parameters on the adsorption process where thereafter studied.

Effect of adsorbent dose was studied by varying the amount of adsorbent (0.1, 0.2, 0.4, 0.6, 0.8, and 1 g).

Effect of pH was studied at by varying the pH of the metal ion solution from 3 to 9 using 0.1 M NaOH and 0.1 M HCl for adjustment of pH as appropriate at optimum dose.

Effect of metal concentration was studied by varying the metal ion concentration (5, 50, 100, 150, and 200 mg/L).

Effect of contact time on the uptake of Cd^{2+} and Cr^{6+} by ATK and UTK was investigated by varying the time of

adsorption from 30, 60, 120, 150, and 180 minutes at optimum experimental conditions.

Equilibrium data obtained was analyzed using isotherm models (Langmuir, Freundlich, and Temkin).

2.5.1. Kinetic Experiment. Batch kinetics was carried out on the removal of the two metal ions from aqueous solutions. The aqueous sample was taken at different time intervals (30, 60, 120, 150, and 180 minutes), and the residual concentration of metal ions was determined using AAS. The amount adsorbed at time t , q_t (mgg^{-1}) was calculated using the following equation [14]:

$$q_t = \frac{C_o - C_t}{m} V. \quad (3)$$

3. Results and Discussion

3.1. Characterization of Cola Nut Leaves. The prominent vibration band shown in the FTIR Spectrum of cola nut leaves is presented in Table 1. The functional groups and their corresponding wave length are given in the table. These functional groups also participated in the adsorptive studies supporting a physisorption mechanism [15].

The FTIR results for the leaves before and after adsorption show slight change in the wavelength (Δcm^{-1}), but does not result in the formation of a new functional group. This slight change could be as a result of electronic interaction. In such cases, the type of bonding that has taken place is a physical bonding, where no new bond is formed. The FTIR analysis shows that the reaction taking place is a physisorption reaction. Some of the characteristics of the physisorption reaction include particles are strongly mobile on the surface of the adsorbent because they are relatively far from the surface plane due to the low binding energy and such reaction requires low desorption temperature [17]. A similar result was obtained by Ajaelu and Dawodu. [15], for the biosorptive removal of nickel (II) by *Mangifera indica* seed.

3.2. Effects of Operational Parameters on the Removal of Cd^{2+} .

Effect of adsorbent dose is carried out in order to maximize the interaction between the adsorbent and metal ions. The effect of biosorbent dose on Cr (VI) ion adsorption onto ATK and UTK is presented in Figure 1. The percentage removal increased from 99.86–99.99% for ATK and 95.89–99.39% for UTK as biosorbent dose increases from 0.1–1 g. Figure 2 shows the plot of percentage removal of Cd^{2+} metal ions against varying amounts of ATK and UTK. The result indicated that the percentage removal of Cd (II) ions increases with increasing adsorbent doses as also observed by Ogunsile and Babarinde [18] with a removal efficiency of 99.30 to 99.80% for ATK and 99.00 to 99.50% for UTK, thereafter maintaining equilibrium. The removal efficiency of the metal ions depends on quantity of the biosorbent. The increase in percentage removal of Cd (II) and Cr (VI) ions with increase in adsorbent dose was due to the

availability of more adsorbent surfaces for the solutes to be adsorbed.

The effect of pH on Cr (VI) and Cd (II) ion adsorption is presented in Figures 3 and 4, respectively. pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of the adsorbent and the degree of ionization of the heavy metal in the solution [19]. At low pH, the surface of the biomass would be protonated and would therefore repel Cr and Cd ions [20]; hence, the sorption of metal ion is minimal. Increasing the pH resulted in increase in the number of negatively charged sites that favored the electrostatic attraction [21] of the Cr (VI) and Cd (II) ions. Leyva et al. [22] reported a similar result for the adsorption Co (II) ions onto activated carbon. Complexation and precipitation of metal could take place in the solution, if contact between adsorbent and adsorbate is low [23]. Hence, the formation of complexes was minimized by increased amount of adsorbent (1 g) used and increased concentration of adsorbate. Furthermore, according to Gonçalves et al. [24], the tendency of ion capture by adsorbent as a result of pH could be explained by association and dissociation of some functional groups, e.g., carboxyls, where most carboxyl groups are undissociated in low pH levels, but can participate in complex reactions, while increased pH rate results in functional groups (carboxyls) having negative charges and therefore may attract positive charged ions. The maximum removal efficiency for the adsorption of Cd ions was 96.85% and 96.36% for both ATK and UTK adsorbents, respectively, at an optimum pH of 9.0.

Consequently, the working pH value for Cr (VI) ions removal onto ATK and UTK was chosen as 8.0, which was also obtained by Antunes et al. [25] in their research.

The effect of varying concentration of Cr (VI) and Cd (II) ion on adsorption onto ATK and UTK is shown in Figures 5 and 6, respectively. The percentage removal increased as the initial concentration of metal ions increased until equilibrium was reached. According to Dang et al. [26], this result is expected, as the concentration serves as a motivating force to surmount mass transfer resistances linking the aqueous and solid phases. It can also be depicted that, increase in the initial metal ion concentration resulted in increase in number of collisions among the metal ion and the biosorbent. The initial Cr (VI) and Cd (II) ions concentration was varied from 5.00–200.00 mg/L under optimum conditions, and the optimum value of Cr (VI) ion adsorption was observed at 99.99% for ATK and 99.99% for UTK, as shown in Figure 5. Also, for Cd (II), as the concentration increased, the amount of Cd (II) ions adsorbed also increased up to 50 mg/L, after which no net adsorption occurred. It can be depicted that increasing the initial concentration increased the sorption gradient, and hence percentage removal increased. After the initial concentration of 50.00 mg/L, biomass saturation occurred, and the biomass attained equilibrium.

The increase in the quantity of metal ion uptake can also be as a consequence of increased collision between metal ions and the surface of the biosorbent and increased rate of metal ions diffusion onto the biosorbent surface [27] due to

TABLE 1: FTIR analysis of cola nut leaves before and after adsorption with their corresponding functional groups [16].

S/N	Vibration peaks of cola nut leaves before adsorption (cm^{-1})	Functional groups	Vibration peaks of cola nut leaves after adsorption (cm^{-1})	Change in wavelength (Δcm^{-1})
1	3384.4	O-H	3276.3	108.1
2	2922.2	C-H ₂ stretching	2918.5	3.7
3	2855.1	CH ₃	28561.4	3.7
4	1733.2	C-O-O-CO- saturated acid anhydride	1729.5	3.7
5	1449.2	N-N=O	1438.8	7.4
6	1375.4	CH ₃ symmetrical deformation	1315.8	59.6
7	1162.9	S group of C=S	1148.0	14.9
8	1066.0	C-O stretch	1032.5	33.5

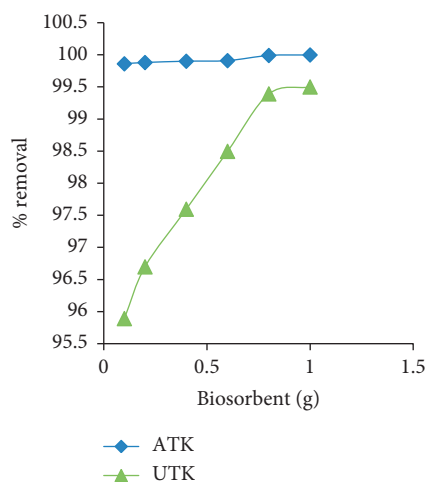


FIGURE 1: % removal of Cr (VI) ions versus biosorbent dose.

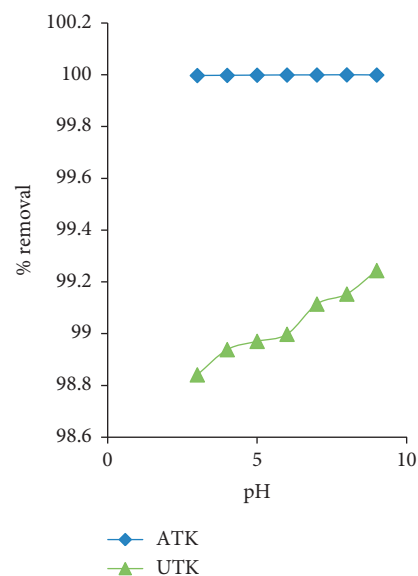


FIGURE 3: % removal of Cr (VI) ions versus pH.

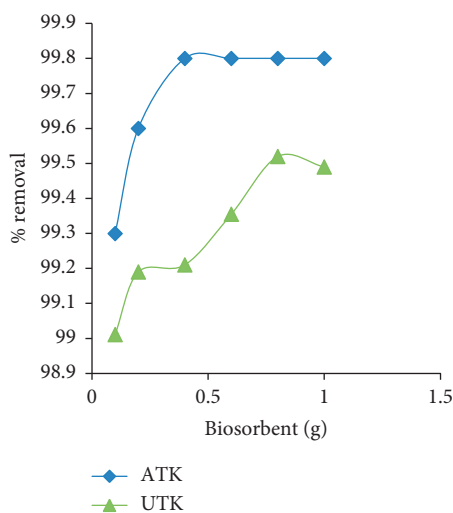


FIGURE 2: % removal of Cd (II) ions versus biosorbent dose.

availability and accessibility of vacant site for metal ion adsorption. Hence, equilibrium is established, as the active sites of both biosorbents attained saturation point and no additional adsorption [28].

The effect of contact time on Cr (VI) and Cd (II) ion adsorption onto ATK and UTK is presented in Figures 7 and

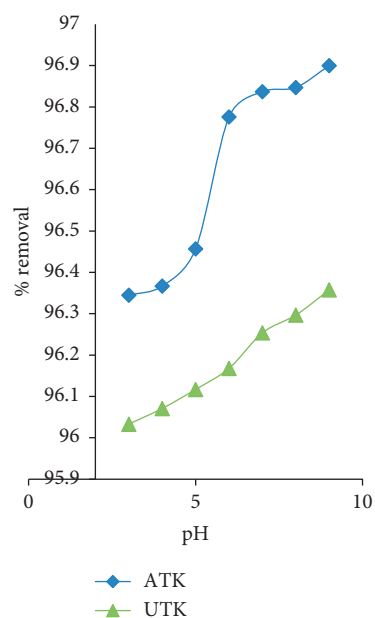


FIGURE 4: % removal of Cd (II) ions versus pH.

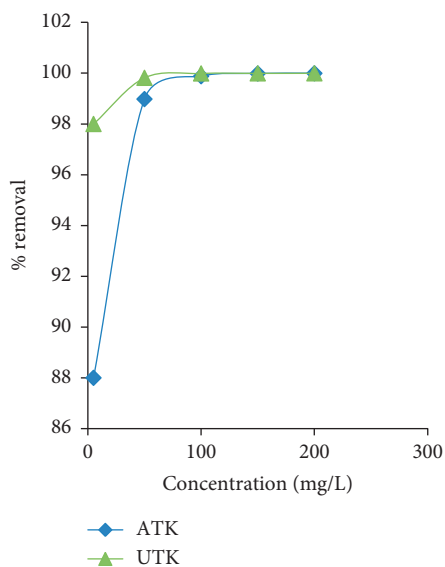


FIGURE 5: % removal of Cr (VI) ions versus concentration.

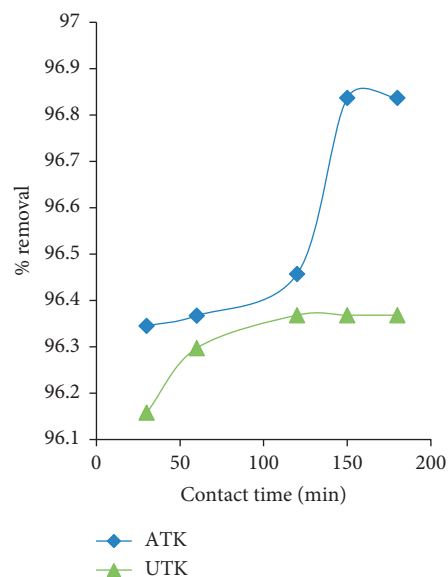


FIGURE 7: % removal of Cr (VI) ions versus contact time (mins).

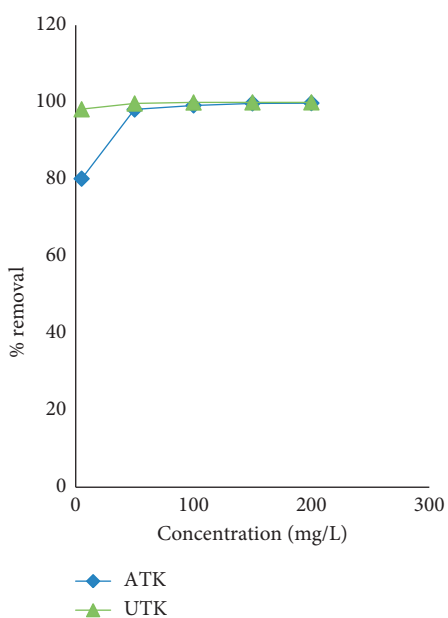


FIGURE 6: % removal of Cd (II) ions versus concentrate.

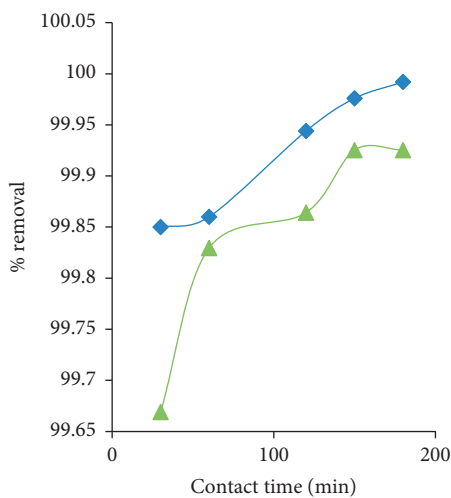


FIGURE 8: % removal of Cd (II) ions versus contact time.

8, respectively. It can be clearly observed that the percentage adsorption generally increased until the time reached 150.00 minutes for ATK and UTK. The removal of Cd (II) ions increased from 99.85–99.99% for ATK and 99.67–99.93% for UTK as time increases from 30–180 minutes. It is clearly observed that the percentage adsorption of Cr (VI) ion gradually increased until time reached 150.00 minutes for ATK and UTK. After this time, there was slight decrease in the adsorption percentage. Thus, 150 minutes was chosen as the optimum time. The highest percentage of adsorption was found to be 96.83% for ATK and 96.37% for UTK. Thereafter, the surface adsorption sites became exhausted, and the removal of metal ion is

controlled by the rate at which the adsorbate is moved from the exterior to the inner sites of the biomass particles [29]. Similar results were reported using wheat shell as the biosorbent.

3.3. Biosorption Kinetics. The adsorption kinetics of Cd^{2+} and Cr^{6+} was investigated to establish the rate of mechanism of the adsorption process. Pseudo-first-order and pseudo-second order are the rate equations that were used to analyze the experimental data. The evaluated kinetics parameters obtained from the linear plots of the models (Figures 9(a)–9(h)) are presented in Table 1 for the adsorption of Cd^{2+} and Cr^{6+} .

3.3.1. Pseudo-First-Order Kinetics. The pseudo-first-order equation (Lagergren's equation) describes adsorption according to the adsorption capacity of solid. The model

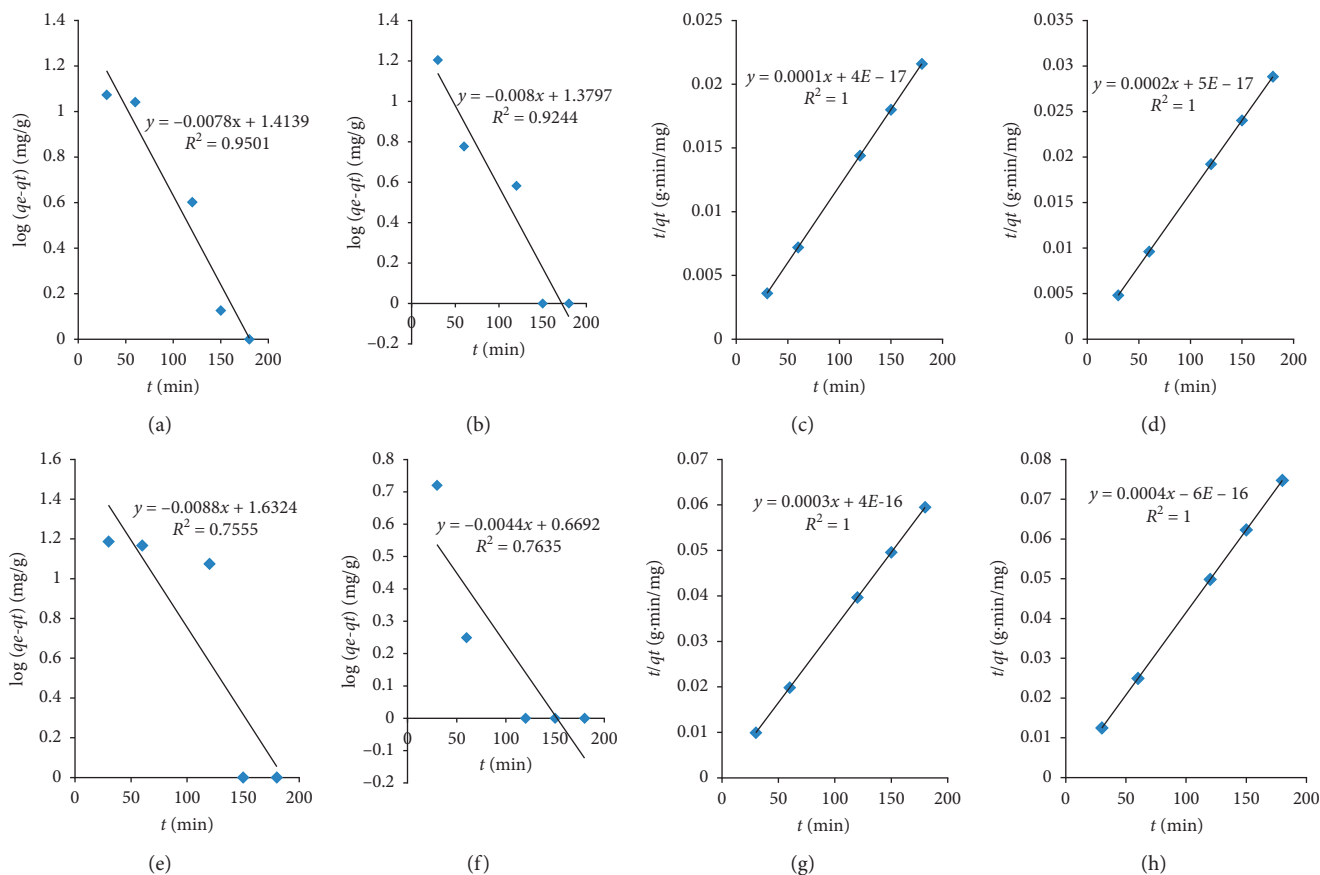


FIGURE 9: Linear plots of (a) pseudo-first-order and (b) pseudo-second-order for Cd^{2+} adsorption by ATK and (c) pseudo-first-order and (d) pseudo-second-order for Cr^{6+} adsorption by ATK. Linear plots of (e) pseudo-first-order and (f) pseudo-second-order for Cd^{2+} adsorption by UTK and (g) pseudo-first-order and (h) pseudo-second-order for Cr^{6+} adsorption by UTK.

assumes that one metal ion is adsorbed on one site of the adsorbent surface [14].

The linear equation of pseudo-first-order is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (4)$$

where q_e is the amount of metal ion adsorbed at equilibrium per unit weight of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$), q_t is the amount of metal ion adsorbed at any time (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1})

The plot of $\log(q_e - q_t)$ versus t gives a linear relationship and k_1 and q_e were obtained from the slope and intercept of the plot.

3.3.2. Pseudo-Second-Order Kinetics. The model assumes that one metal ion is adsorbed onto two sorption sites on the adsorbent surface [14]. The pseudo-second-order linear expression is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (5)$$

where k_2 is the rate constant of pseudo-second-order adsorption ($\text{g}/\text{mg}\cdot\text{min}$).

Based on the evaluated parameters of the pseudo-first-order model of Cd (II) ions biosorption onto ATK and UTK biosorbents, q_e values indicated that biosorbents adsorbed more Cd (II) ions within a short contact time and the correlation of determination, and R^2 values indicated that the biosorption of Cd (II) ion onto the two biosorbent fits pseudo-first-order due to good correlation between $\log(q_e - q_t)$ and t . Also, the correlation parameters of the pseudo-second-order model of Cd (II) ion biosorption onto ATK and UTK biosorbents shows R^2 value that suggests the biosorption of Cd (II) ion onto the two biosorbents fits best into the pseudo-second-order model than pseudo-first-order due to better correlation between t/q_t and t , as shown in Table 2. Similar results were obtained by Wang et al. [27].

Table 2 also shows the correlation parameters of the pseudo-first-order and pseudo-second-order model of Cr (VI) ions biosorption onto ATK and UTK biosorbents. The q_e (5.1161 mg/g for ATK and 1.9527 mg/g for UTK) values indicated that less amount of Cr (VI) ions were adsorbed within a limited time, and the correlation of determination of R^2 (0.7555 for ATK and 0.7635 for UTK) suggested that biosorption of Cr (VI) ions fit into the pseudo-first-order model. Also, the q_e (4.1120 mg/g for ATK and 3.9737 mg/g for UTK) values indicated less amount of Cd (II) ions adsorption with good correlation value R^2 (0.9501 for ATK and

TABLE 2: Evaluated parameters of pseudo-first-order and pseudo-second-order for Cd (II) and Cr (VI) metal ion biosorption onto ATK and UTK.

Model	Adsorbent	q_e (mg/g)	k_1 (min^{-1})	R^2
Pseudo-first-order	ATK for Cd^{2+}	4.1120	0.018	0.9501
	UTK for Cd^{2+}	3.9737	0.0184	0.9244
	ATK for Cr^{6+}	5.1161	0.0202	0.7555
	UTK for Cr^{6+}	1.9527	0.0101	0.7635
Pseudo-second-order		q_e (mg/g)	k_2 (g/mg min)	R^2
	ATK for Cd^{2+}	1.45	2.303	1
	UTK for Cd^{2+}	1.453	4.609	1
	ATK for Cr^{6+}	0.034	6.909	1
	UTK for Cr^{6+}	1.345	9.212	1

0.9244 for UTK), which suggest that biosorption of Cd (II) ions fits into the pseudo-first-order model. The pseudo-second-order model shows the correlation value, R^2 (1.00 for ATK and 1.00 for UTK biosorbents) for the adsorption of both Cr (VI) and Cd (II) ions, which fits into the pseudo-second-order model than the pseudo-first-order model due to better correlation between t/q_t and t , as also described by Igwe et al. [30].

3.4. Adsorption Isotherm. The adsorption isotherm is an expression which gives a relationship between the quantity of solute adsorbed and the amount of solute residual in a given solution. Langmuir, Freundlich, and Temkin isotherms have being used to analyze the equilibrium adsorption models. The Langmuir isotherm model explains a monolayer coverage of the solute on a uniform surface of an adsorbent and that saturation coverage is the complete use of the binding sites [12], which can contain only one adsorbate. The equation for the linear Langmuir isotherm is given as

$$\frac{C_e}{q_e} = \frac{1}{q_0} C_e + \frac{1}{K_L q_0} \quad (6)$$

The Langmuir isotherm constant K_L ($\text{L}\cdot\text{mg}^{-1}$) R_L , which is a dimensionless constant, and other parameters are used to evaluate the Langmuir isotherm from the linear plot of C_e/Q_e against C_e .

The Freundlich isotherm model describes both monolayer and multilayer. It assumes heterogeneity and the exponential distribution of active sites and their energies [14]. The linear form of the Freundlich equation is given as

$$\log q_e = \log K_F + \log \frac{1}{n} C_e \quad (7)$$

The Freundlich isotherm constants and K_f sorption intensity (n) are parameters characteristic of the Freundlich isotherm used for evaluation, obtained from the linear plot of $\log Q_e$ against $\log C_e$.

The Temkin isotherm contains a factor that clearly takes into account of adsorbent-adsorbate interactions. The model assumes that heat of adsorption for all molecules in a layer would decrease linearly rather than logarithmic with coverage [31]. The linear equation for plot of q_e against in C_e is

$$q_e = \frac{RT}{b_T \ln A} + \frac{RT}{b_T \ln C_e} \quad (8)$$

Table 3 shows the correlation parameter of the Langmuir isotherm for Cd (II) ions biosorption onto ATK and UTK biosorbents. R_L (0.0046 for ATK and 0.0064 for UTK biosorbents) indicates that the biosorption of Cd (II) ion by biosorbents was favourable and coefficient of determination, R^2 (0.3707 for ATK and 0.1803 for UTK), signifies that the biosorption does not fit into the Langmuir isotherm.

Table 3 shows the Freundlich isotherm constants and correlation coefficient for Cd (II) ions biosorption onto ATK and UTK biosorbents, n (0.3749 for ATK and 0.3966 for UTK biosorbents) values indicated favourable biosorption (since $1/n < 1$), and R^2 (0.5617 for ATK and 0.6256 for UTK biosorbents) values indicated that sorption of Cd (II) ions onto biosorbents fit into the Freundlich isotherm than Langmuir.

Table 3 also shows the correlation parameter of the Langmuir isotherm for Cr (VI) ions biosorption onto ATK and UTK biosorbents. R_L (0.000599 for ATK and 0.000111 for UTK biosorbents) values indicated that the biosorption of Cr (VI) ion onto UTK biosorbents was favourable, and R^2 (0.548 for ATK and 0.5258 for UTK biosorbents) values show that the process of Cr (VI) ion adsorption onto ATK biosorbent fit into the Langmuir isotherm as also described by Wang et al. [27].

Table 3 shows the Freundlich isotherm constants and correlation coefficient for Cr (VI) ions biosorption onto ATK and UTK biosorbents. R^2 (0.6477 for ATK and 0.6985 for UTK biosorbents) values indicated that biosorption of Cr (VI) ions onto UTK biosorbent fit into the Freundlich isotherm.

The Temkin isotherm model describes b_T as a constant which is related to the heat of adsorption and A_T as the equilibrium binding constant (Lg^{-1}). Table 3 shows the low heat of adsorption, which is an indicator of a physorption type of reaction and the low binding energy. The R^2 values obtained from the Temkin isotherm indicate better correlation when compared to other isotherms tested. Adsorption of Cd ion by UTK does not fit into the model, while Cr can best be described by the Temkin isotherm.

Table 4 shows the maximum adsorption capacity of some adsorbents used for the adsorption of Cd and Cr ions. It can be seen that cola nut leaves have high amount of q_m , therefore being a good adsorbent.

TABLE 3: Evaluated parameters of Langmuir, Freundlich, and Temkin isotherms for Cd (II) and Cr (VI) metal ion biosorption onto ATK and UTK.

Model	Biosorbents	Q_o (mg/g)	K_L (L/mg)	R_L	R^2
Langmuir	ATK for Cd ²⁺	178.57	2.15	0.0046	0.3707
	UTK for Cd ²⁺	555.56	1.56	0.0064	0.1803
	ATK for Cr ⁶⁺	200	16.67	0.000599	0.548
	UTK for Cr ⁶⁺	185.19	899.97	0.000011	0.5258
Freundlich		K_f		N	R^2
	ATK for Cd ²⁺	17.972		0.3749	0.5617
	UTK for Cd ²⁺	218.85		0.3966	0.6256
	ATK for Cr ⁶⁺	13.129		1.5035	0.6477
	UTK for Cr ⁶⁺	5.0298		1.058	0.6985
Temkin		b_T	A_T (Lg ⁻¹)	B	R^2
	ATK for Cd ²⁺	0.00123	1.219	6784.7	0.855
	UTK for Cd ²⁺	0.0025	295.35	404.91	0.1299
	ATK for Cr ⁶⁺	0.0065	1.10	1280	0.9553
	UTK for Cr ⁶⁺	0.0064	6.380	1303.3	0.7828

TABLE 4: q_m of various adsorbents for the removal of Cd (II) and Cr (VI) ions.

Adsorbent used for the removal of metal ions from solution	Type of metal ion adsorbed	Maximum monolayer adsorption capacity (q_m mg/g)	Reference
Activated coal	Cr III	13.552	[23]
Oxidized MW carbon nanotubes	Cr VI	4.262	[32]
<i>Rhizopus arrhizus</i> for removal	Cr VI	23.92	[33]
Dried activated sludge	Cd II	84.30	[34]
<i>Tamarindus indica</i> seeds	Cr VI	0.098	[35]
Coconut copra meal	Cd II	4.92	[36]
Crude tamarind fruit shells (CTFS)	Cr VI	74.62	
HCl-treated shells (H-TS)	Cr VI	140.84	[37]
Oxalic acid-treated shells (O-TS)	Cr VI	151.51	
Orange peels	Cd II	123.65	[38]
Pinus bark	Cd II	10.384	[24]
Pinus bark	Cr VI	-10.661	
ATK cola nut leaves	Cr VI	178.57	
UTK cola nut leaves	Cr VI	555.56	
ATK cola nut leaves	Cd II	200	
UTK cola nut leaves	Cd II	185.19	

4. Conclusions

In this research, the adsorption of Cd II and Cr VI using cola nut leaves biomass was studied. The investigation of the equilibrium sorption was carried out at room temperature. The study revealed that adsorption of Cd (II) ions and Cr (VI) ions onto acid-treated and untreated leaves depended on the operational parameters. It can also be depicted that the untreated cola nut leaves have high adsorption capacity compared to other adsorbents. The pseudo-second order model best described the kinetics of the biosorption of the metal ions. The sorption data fitted into Langmuir, Freundlich, and Temkin isotherm models and were better described by the Temkin model. It can be concluded that leaves of cola nut tree are a potential and active biosorbent for removal of cadmium and chromium ions from its aqueous solution and can thereby serve as a bioremediator in industrial waste water treatment.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

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