

Research Article

Removal of Chromium (VI) from Aqueous Environment Using Modified *Parkia Biglobosa* (Locust Bean) Shell

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Abstract

The different metal complexing ligands containing synthetic and natural adsorbents have been described in literature for the removal of heavy metal ions from aqueous solutions. However, the removal of Chromium (IV) ion using *Parkia biglobosa* is yet to be reported in literature. A new method was developed to obtain adsorption capacity using modified *Parkia biglobosa* shells as a natural Chromium (IV) heavy metal ion adsorbent from aqueous solution at a certain pH. Agricultural waste: Carob husks (a product derived from carob beans) were modified with HNO₃ and citric acid, and their effectiveness on the removal of Cr (VI) from aqueous solutions was examined in a batch experiment. The core sizes used are 150 μm and 300 μm . The effects of different parameters such as pH, Cr (VI) concentration, adsorbent loading, and contact time were determined. The optimum pH values for the two dimensions were found to be 3 and 1, respectively. The contact time for maximum adsorption is 30 minutes. The Freundlich isotherm describes the equilibrium between liquid and solid phases. *Parkia biglobosa* can be said to be a good adsorbent for the removal of Chromium (VI) heavy metal ion from aqueous solutions depending on the pH of the solution.

Keywords

Parkia Biglobosa, Wastewater Treatment, Adsorption, Heavy Metal Removal, Water Purification

1. Introduction

The importance of using local materials to produce adsorbents in developing countries such as Nigeria cannot be overemphasized. The cost of the raw material is less than the cost of importing adsorbents. Commercial adsorbents such as alumina, activated carbon, zeolites, and silica are not only expensive but difficult to reproduce. Chromium needs to be adsorbed from water or wastewater containing chromium. Chromium IV is one of the heavy metal ions that is toxic to aquatic plants and animals [19]. These pollutants are released when emission thresholds are exceeded. For groundwater, the maximum concentration in clean water is 0.1 mg/L and

0.05 mg/L [15]. There are many ways to remove heavy metal ions from contaminated water. These processes are lime coagulation, chemical precipitation, solvent extraction, reverse osmosis, and ion exchange. This technology, combined with electronic equipment and high-pressure reagents, enabled the unbiased removal of metal ions. Additionally, this technology is quite expensive to use. To solve these problems, an environmentally friendly and effective method that will reduce the concentration of heavy metal ions in water or wastewater needs to be evaluated. We need to create a good and effective environment to reduce heavy metals. In recent

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years, significant research has been conducted on biosorption to remove unnecessary heavy metals from wastewater before they are released into the environment. Heavy metals in aqueous solutions at different concentrations can bind and activate certain inactive and non-living microbial biomasses. The ability of these chemicals to bind to heavy metals and condense is called biosorption. This biological phenomenon involves the ion exchange of some bacteria, fungi and algae. The use of solids to produce high-performance and low-cost adsorbents for the removal of heavy metals in wastewater has been reported in literature. Results of chromium adsorption from wastewater using modified solids were reported by Ugoke et al. [3]. The results showed that such agricultural waste can remove heavy metals. Adeyemi and Dauda [5], used crushed soybeans to remove lead (II) ions from aqueous solutions. Adsorption occurs more easily with isothermal adsorption and the kinetics obtained from their studies. Therefore, it can be concluded from the results that ligno-cellulosic carob bark effectively removes heavy metal ions from pollutants. Nathaniel et al. [7] showed that the use of modified soybeans could chelate nickel and aluminum ions from aqueous solutions. Jeje et al. [6] in their study on the adsorption capacity, kinetics and thermodynamics of activated and unactivated carob shells showed that heat is absorbed (endothermic reaction) and the reaction kinetics is pseudo-second order. The results also showed that lead ions can be removed from the contaminant using carob bark. Similarly, Olugbenga et al. [20]; used modified carob shells to remove the rhodamine B dye from the product. Ahalya et al. [8] used agricultural wastes obtained from soybeans (Benga gram husk) to remove chromium (VI) ions. It was concluded that biomass can remove unwanted heavy metal ions. Adamu and Ahmadu. [21] examined the comparative performance of *Parkia biglobosa* and carbon cake in removing heavy metals from wastewater. Vinodhini and Nilanjana. [16], attempted to study the sorption of chromium (VI) using neem wood chips. They reported the important role of lignocellulosic fraction in the removal of chromium (VI) ions through metabolic-mediated or physicochemical absorption pathways. Functional groups in the adsorbent were examined using FTIR (Fourier Transform Infrared Spectroscopy) analysis. Laboratory analysis revealed the presence of C=O and OR groups. In addition, experimental results showed that SO and -CN3 were stretched during the biosorption process. To clearly understand the composition of the precursor, EDX (Energy Dispersive X-Ray Analysis) analysis was performed to examine its main elements. ESR (Electron Spin Resonance) studies on the lignin composition of neem sawdust showed a decrease in chromium oxidation state from (VI) to (III). Therefore, they concluded that adsorption combined with reduction was the mechanism of chromium (IV) biosorption. Parinda et al. [13] studied the adsorption of chromium (IV) ions from aqueous solutions using coconut fiber. In their research, they determined the amount of adsorbent, the pH of the body, and the contact time. The adsorption

capacity and adsorption mechanism of chromium (VI) is the main research topic. Radojka and Marina [14], used waste from tea mushroom biomass to study the influence of various factors on the biosorption of copper (II) and chromium (VI) ions. They studied the properties of dry biomass to remove Chromium ions at different brine concentrations and adsorbent dosages. Dried tea mushroom biomass at a dose of 0.15 g/L has been reported to have Cu (II) uptake up to 38 mg/g and Cr (VI) uptake up to 38 mg/g at 20 °C. 33 mg/g when dried at 80 °C. mg/g. Additionally, they showed that biomass dried at high temperatures showed better biosorption of chromium ions, while biomass dried at low temperatures showed better biosorption of copper ions.

Agricultural wastes have good adsorption performance for heavy metal ions due to their versatility in different operating conditions, concentration independence, high regeneration tendency, high tolerance to organic matter, high metal selectivity towards metal salts and are affected by the environment. minor Alkaline earth metals and related metals. At the same time, the performance of these waste products is improved by chemical and other modifications. This modification process helps improve the binding properties of the adsorbent. Although the production cost of the adsorbent increases, the efficiency of the adsorbent increases.

Vinodhini and Nilanjana [17]; Muhammad and Prasad [11]; Modrogoan et al. [10]; Olayinka et al. [12] and Ahalya et al. [8] used agricultural wastes as adsorbents at different times to adsorb heavy metal ions in wastewater. However, there are few reports on the use of carob bark powder to adsorb chromium (VI) ions.

2. Materials and Methods

Mature carob bark was collected from carob trees behind the boys' dormitory of the Federal University of Technology, Minna. main campus. The leaves were dried in a cool place at room temperature until crisp. The dried leaves are finally pulverized and graded through a series of sieves with a mesh size of 100 to 400 μm . 150 and 300 μm powder were collected, and stored in clean nylon bags. Approximately 200 g each was mixed with 200 ml of 0.5 mol/dm³ HNO₃, and stirred the mixture for two minutes. Each small piece was washed with distilled water until it becomes colorless and strong for adsorption on the shell. The pH of the cleaning solution was about 6.9. Each small piece was separated with filter paper and funnel. The adsorbent was dried at 60 °C for 24 hours. The adsorbent was pulverize using a pestle and mortar. The adsorbent was then treated with 0.5 mol dm⁻³ citric acid for further modification using the same method as described above. All chemicals used in this study were of analytical grade and all solutions were prepared from deionized water. K₂CrO₄ is used as the Cr(VI) source. 3.7203g K₂CrO₄ was dissolved in 1L of deionized water to prepare 1000mg/L chromium stock solution. Different synthetic samples with different chromium concentrations were prepared from the solutions by appropriate dilution. The pH of the aqueous

solution was adjusted to the desired level by adding 1 M NaOH solution. Biosorption is done in a batch system. The effect of contact time was examined by adding 0.5 g of sorbent to 40 ml of 5 mg/L and shaking at 180 rpm with an IKA HS 260 simple piston shaker, at different times. The mixture was filtered using Whatman No. 1 Filtered paper, and the filtrate were analyzed at 357.87 nm using Flame Atomic Absorption (FAAS) Perkin Elmer A Analyst 200 to obtain residual chromium present. The effect of dose on ion adsorption was investigated. 0.5-2.5 g was weighed, and put into an Erlenmeyer flask. A 40 mL of 10 mg/L metal solution was shaken for 60 min, filtered, and measured the adsorbed metal ions. To determine the effect of metal ion adsorption content, 0.5 g of adsorbent was added to 40 ml of metal ion solution at different concentrations (10 - 50 mg/L). The mixture was shaken for 60 min, filtered, and the concentration of adsorbed metal ions was determined. The effect of pH on ion adsorption was examined by adjusting the pH of the solution between 1 and 5, using 0.5 g of adsorbent and 40 mL of 10 mg/L solution. The mixture was shaken for 60 min, filtered, and the amount of adsorbed ions was determined. The relationship between the degree of biosorption is as follows:

$$(\% \text{removal}) = \frac{C_o - C_t}{C_o} * 100 \quad (1)$$

The amount of Cr (VI) adsorbed per unit mass of the adsorbent is given by equation 2,

$$q \text{ in mg/g} = C_o - C_t * V/m \quad (2)$$

Table 1. Values of Parameter Investigated.

Parameters	Values
Particle Size (μm)	150 and 300
Concentration (mg/L)	10, 20, 30, 40 and 50
Ph	1, 2, 3, 4 and 5
Adsorbent Loading (g)	0.5, 1, 1.5, 2.0 and 2.5
Contact Time (min)	30, 60, 90, 120 and 150

Table 1, shows the values of the investigated parameters at different proportions.

2.1. Adsorption Isotherm Model

Freundlich adsorption isotherm is expressed as

$$q_e = K_f C_e^{1/n} \quad (3)$$

Where K_f relates to sorption capacity and n to sorption intensity

The logarithmic form of Eq. (3) given below is usually used

to fit data from batch equilibrium studies:

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log } C_e \quad (4)$$

The Freundlich Isotherm Coefficients are determined by plotting $\text{Log } q_e$ versus $\text{Log } C_e$. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface [12].

The Langmuir model for adsorption is:

$$q_e = \frac{abC_e}{1+bC_e} \quad (5)$$

where q_e = amount of adsorbate adsorbed per unit mass of solid (mg/g), b = Langmuir adsorption constant related to the energy of adsorption (l/mg), a = maximum adsorption capacity of the solid (mg/g), C_e = equilibrium solution concentration of the adsorbate (mg/l) [2].

2.2. Surface Area Determination

The surface area of the carob bark adsorbent was determined by the iodine adsorption method. The amount of iodine absorbed from the aqueous solution is estimated by titrating the blank with standard thiosulfate solution and comparing it with the titration of the iodine-containing carob bark sample. The indicator used is starch. Surface area (mg/g) is calculated as follows;

$$= \frac{(V_{\text{blank}} - V_{\text{sample}}) * N * 40 * 127}{V_{\text{blank}} * W}$$

Where;

V_{blank} = Volume of blank used

V_{sample} = Volume containing adsorbent

N = Normality of iodine

W = Weight of adsorbent used

3. Result

Physicochemical Properties of Adsorbent

Selected characteristics of the adsorbent were investigated and are presented in Table 2.

Table 2. Physicochemical characteristics of the adsorbent.

Parameters	Adsorbent
Surface Area (mg/g)	1172.31
Ash Content (%)	3.5
Bulk density (g/cm ³)	1.073

Table 2, shows the physicochemical characteristics of the adsorbent obtained from Proximate and BET analysis.

3.1. Effect of Contact Time on the Adsorption of Metal Ion

Co = 5 mg/L, W = 0.5 g, V = 40 ml, dp = 150 μ m

Table 3. Effect of contact time on adsorption of metal ion (Initial conc. (Co) = 5 mg/L).

Contact time (min)	Concentration left (mg/L) Ca	Concentration removed (mg/L) Cb	% Removal
30	1.126	3.874	77.480
60	2.010	2.990	59.800
90	1.432	3.568	71.360
120	1.195	3.805	76.100
150	1.273	3.727	74.540

Co = 5 mg/L, W = 0.5 g, V = 40 ml, dp = 300 μ m

Table 3 shows the variation in the concentration of Ca left and Cb removed as contact time increases. Table 3 and 4 shows that as the contact time increases, the metal ion adsorption increases.

Table 4. Effect of contact time on metal ion adsorption (Initial conc. (Co) = 5 mg/L).

Contact time (min)	Concentration (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
30	0.863	4.137	82.740
60	2.706	2.294	45.880
90	2.215	2.785	55.700
120	2.074	2.926	58.520
150	1.235	3.765	75.300

Table 5. Effect of Adsorbent Loading on the Adsorption of Cr (VI) (Co = 10 mg/L, V = 40 ml, t = 60 min, dp = 150 μ m).

Mass (g)	Concentration left (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
0.5	1.824	8.176	81.760
1.0	1.587	8.413	84.130
1.5	1.706	8.294	84.940
2.0	1.453	8.547	85.470
2.5	0.497	9.503	95.030

Co = 10 mg/L, V = 40 ml, t = 60 min, dp = 300 μ m

Table 6. Effect of adsorbent loading on the adsorption of Cr (VI) (Initial conc. (Co) = 10 mg/L).

Mass (g)	Concentration left (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
0.5	1.323	8.677	86.770
1.0	1.128	8.872	88.720
1.5	1.320	8.680	88.800
2.0	1.034	8.966	89.660
2.5	1.034	8.966	89.660

3.2. Effect of Concentration on Metal Ion Adsorption

V = 40 ml, t = 60 min, dp = 150 μ m, W = 0.5 g

Table 5 and 6: shows that as the adsorbent loading increases, the capacity of the adsorbent to remove the ion, increases.

Table 7. Effect of concentration on metal ion adsorption.

Concentration (mg/L), Co	Concentration left (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
10.0	0.949	9.051	90.510
20.0	1.876	18.124	90.620
30.0	2.071	27.929	90.897
40.0	3.303	36.697	91.743
50.0	6.241	43.759	92.518

v = 40 mL, t = 60 min, dp = 300 μ m, W = 0.5 g

Table 8. Effect of concentration on metal ion adsorption.

Concentration (mg/L), Co	Concentration left (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
10.0	1.039	8.961	89.610
20.0	1.815	18.185	90.925
30.0	2.575	27.425	91.417
40.0	3.126	36.874	92.185
50.0	5.619	44.381	88.762

Increase in concentration result to a corresponding increase in the ion removal as shown in Tables 7 and 8.

3.3. Effect of pH on Metal Ion Adsorption

$v = 40$ mL, $t = 60$ min, $dp = 150$, μm $W = 0.5$ g, $Co = 10$ (mg/L)

Table 9. The effect of pH on Cr (VI) adsorption.

pH	Concentration left (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
1.0	2.137	7.863	78.630
2.0	2.257	7.743	77.430
3.0	1.705	8.295	76.950
4.0	2.400	7.600	76.000
5.0	2.202	7.798	76.080

$V = 40$ mL, $t = 60$ min, $dp = 300$ μm , $W = 0.5$ g, $Co = 10$ (mg/L)

Table 9, shows that increase in pH leads to a decrease in Cr (VI) removal but Table 10, shows a sudden increase in adsorption. This is owed to the taking of record manually.

Table 10. Effect of pH on Cr (VI) adsorption.

pH	Concentration left (mg/L), Ca	Concentration removed (mg/L), Cb	% Removal
1.0	1.571	8.429	84.290
2.0	2.817	7.183	71.830
3.0	2.432	7.568	71.680
4.0	2.326	7.674	70.740
5.0	1.815	8.185	71.850

4. Discussion

The obtained results are as discussed below.

4.1. Effects of Contact Time on the Adsorption of Chromium Ion

The effect of contact time on Cr(VI) adsorption is shown in Figure 1. The adsorption of the two sizes reached the maximum adsorption capacity in the first 30 min (77.48% and

82.74%, respectively). This means that equilibrium is reached quickly and the adsorption sites are saturated to maximum absorption within 30 min [23]. This adsorption percentage drops very quickly. This may be caused by the desorption of metal ions. As reported by Zvinowanda et al. [18], contact time is important for establishing equilibrium during the adsorption–desorption process. An increase in adsorption capacity was observed after 60 min (from 59.8% to 76.1%), then decreased to 74.54 (150 μm) at 150 min, and from 45.88% to 300 μm from 60 min to 150 min. (300 μm) increased to 75.3%. This is because the number of sites is more than the metal ions to be adsorbed [4].

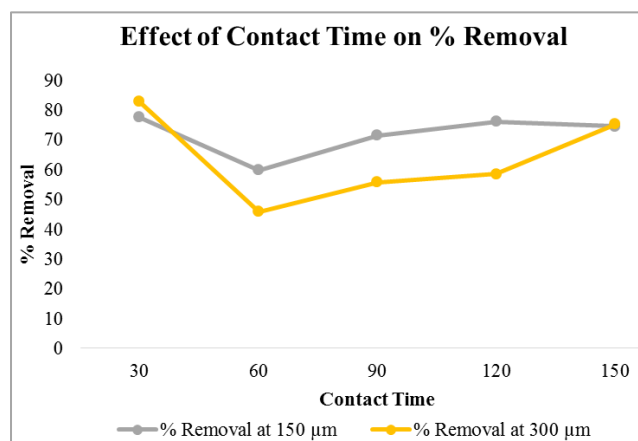


Figure 1. Effect of contact time on adsorption of chromium ion.

4.2. Effect of Adsorbent Loading on the Adsorption of Cr (VI)

The results of the adsorbent loading effect of Cr(VI) are shown in Figure 2. For particles with a particle size of 150 μm , the adsorption rate according to the adsorbent mass increased from 81.76% to 84.13% and changed from 0.5 to 1 g. This is because the positive field created by acid modification is the negative field of Cr(VI) present as chromate in solution. Then, when the adsorbent mass changed to 1.5 g, a sharp desorption of up to 82.94% occurred. This is the result of the separation of the adsorption site, which leads to a decrease in the total adsorbent surface area available for Cr(VI) particles and an increase in the diffusion path length [12]. The adsorption rate quickly increased to 95%. The 300 μm size shows the same behavior except that the percentage of adsorption occurring is higher than that of the 150 μm size, but the adsorption remains constant as at the 2 to 2.5 g size. This is due to the large surface area and the presence of many adsorption sites [4].

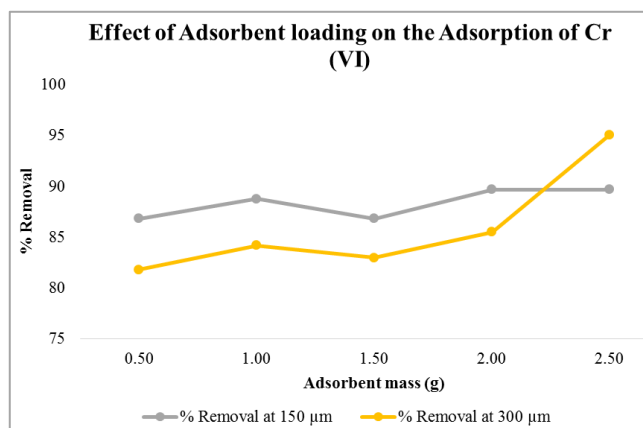


Figure 2. Effect of adsorbent loading on the adsorption of Cr (VI).

4.3. The Effect of Concentration on Metal Ion Adsorption

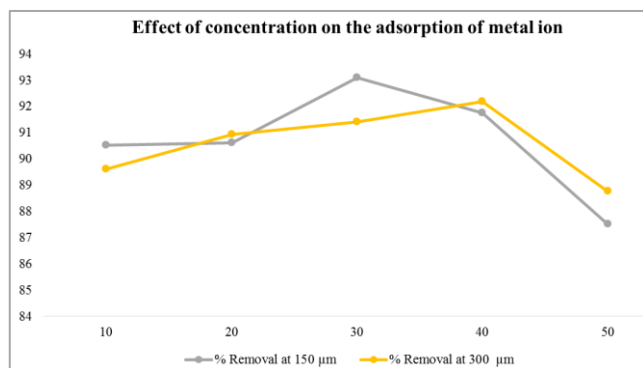


Figure 3. The Effect of concentration on metal ion adsorption.

The effect of different Cr(VI) concentrations on the adsorption capacity is shown in Figure 3 when the other four parameters are unchanged. For the particle size of 150 µm, the adsorption of Cr(VI) ions by the adsorbent increased rapidly, and when the concentration was changed from 10 mg/L to 30 mg/L, the Cr(VI) concentration increased from 90.51% to 93.10%. Comparing the result with the work of Ajayi-Banji et al. [4], the rapid onset of Cr(VI) uptake can be attributed to the interaction between metal ions and active sites of the adsorbent. The adsorption capacity decreases rapidly when the concentration changes from 40 mg/L to 50 mg/L. This is because saturation of the binding site causes metal ions not to be adsorbed at higher concentrations, and further mixing causes desorption. A similar rate was observed for 300 µm particle size, but the

adsorption capacity was lower than 150 µm.

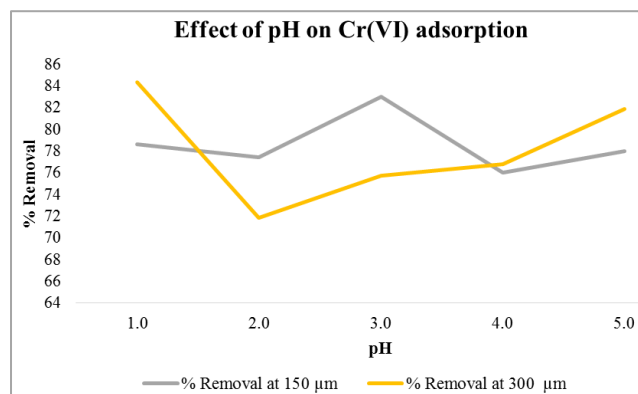


Figure 4. Effect of pH on Cr (VI) adsorption.

pH is an important parameter for the adsorption of metal ions from aqueous solutions as it is related to the solubility of metal ions, the concentration of counter ions on the functional group of the adsorbent, and the degree of ionization of the adsorbates during the time reaction [16]. To examine the effect of pH on Cr removal efficiency, pH was varied from 1.0 to 5.0, as shown in Figure 4. The uptake of the free ion Cr depends on pH; The positive metal removal efficiency tested at pH 1 was reduced to 300. µm and sharply at pH 2. The optimum pH for 150 µm particles is 3, with a rapid decrease at pH 4. Other metals such as chromium (VI) and arsenic are known to exist in anionic form depending on pH. pH plays an important role in the biosorption of Cr (VI) due to the nature of the chemical interaction of each metal with the functional group present on the surface of the adsorbent. At low pH, the total surface charge of the adsorbent is positive, and the negative charge favors the biosorption of $\text{Cr}_2\text{O}_7^{2-}$. Generally, Cr(VI) adsorbs better at low pH. This may be because at low pH, Cr (VI) appears as Cr^{3+} and therefore is better absorbed by the $\text{C}=\text{O}$ functional group of the adsorbent, since oxygen is electronegative and can attract ions well. Additionally, [12] reported that when pH is low, the presence of H^+ neutralizes the negatively charged adsorbent surface, reducing the barrier to dichromate ion diffusion.

4.4. Adsorption Isotherm

The Freundlich Isotherm Coefficients were determined by plotting $\log q_e$ against $\log C_e$ and the results as shown in Table 11.

Table 11. Freundlich and Langmuir Isotherms for different initial concentrations.

Co	Ca	Ce	Qe	log Ce	Logqe	1/Ce	1/qe
10.0	9.000	1.000	0.912	0.0	-0.040	1.000	1.096

Co	Ca	Ce	Qe	log Ce	Logqe	1/Ce	1/qe
20.0	18.095	1.905	1.445	0.3	0.160	0.525	0.692
30.0	27.911	2.089	2.291	0.3	0.360	0.479	0.437
40.0	36.533	3.467	2.884	0.5	0.460	0.288	0.347
50.0	46.019	3.981	3.467	0.6	0.540	0.251	0.288

The Freundlich equation is an empirical equation based on heterogeneous surface adsorption. Constants represent adsorption capacity and adsorption density. The linearity of this graph shows the representative characteristics of the adsorption of the tested adsorbents. The regression coefficient relationship shows that heavy metals are well-adsorbed. The Kf and n values calculated from the slope and intercept of the graph are 0.918 and 1.044, respectively. Kadirvelu et al. [22] stated that, n values between 1 and 10 are considered good adsorbents. Therefore, changing the bn value of PBS to 1.044 means effective adsorption [9]. Experiments: adsorbent dose; 0.5 g, Cr(VI) concentration; 10-50 mg/L, mixing speed; 180rpm.

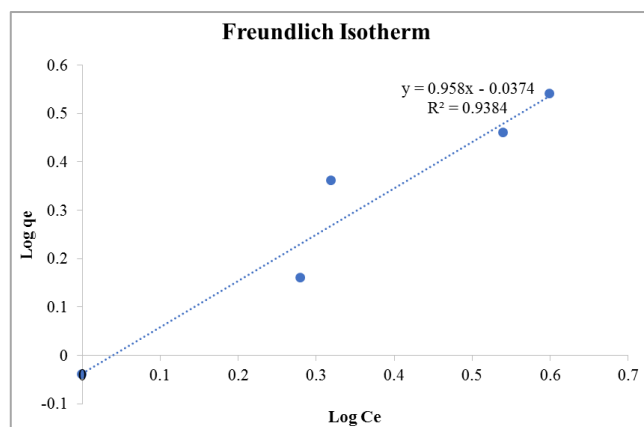


Figure 5. A plot of $\text{Log } q_e$ against $\text{Log } C_e$.

Figure 6 shows the relationship between carob husk size (300 μm) and $1/q_e$ and $1/C_e$ for different initial CO concentrations (10–50 mg/L). The values of (b and a) can be determined as intercept and slope. The data of the Langmuir adsorption isotherm are shown in Table 11. Linear regression analysis of the data is shown in Figure 6 and gives a good fit to the Langmuir adsorption isotherm for different initial concentrations and carob seed shell size (300 μm). The empirical constant and adsorption constant (saturation coefficient) of the Langmuir equation are $a = 45.040 \text{ mg/g}$ and $b = 0.021 \text{ l/mg}$, respectively. The b value can be used to determine $RL = 1/1 + C_{ob}$; where C_o is the initial concentration of the adsorbate. When the RL value is less than 1, the adsorption is positive, and when it is greater than 1, it is nega-

tive [1]. Therefore, adsorption is positive because the RL value is greater than 1 for all C_o values.

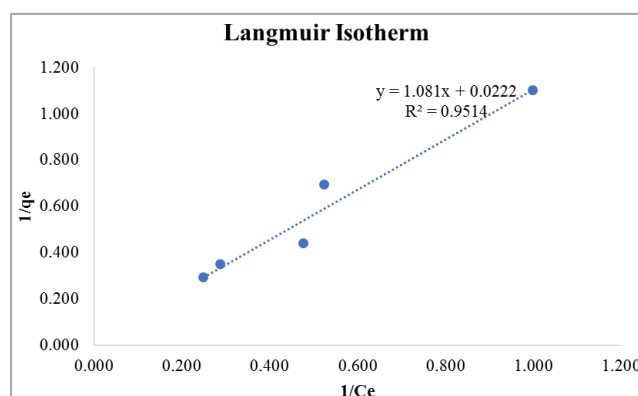


Figure 6. Relationship between $1/q_e$ and $1/C_e$ for locust bean shell size (300 μm) and different initial concentrations C_o (10-50mg/L).

5. Conclusion

The removal of Cr(VI) from aqueous solutions depends on the pH of the solution, sorbent quality, initial concentration, contact time, and particle size. The optimal contact time for both sizes was reached in the first 30 min, while the optimal concentration of Cr(VI) was observed at pH 3.0 for the 150 μm particle size and 1.0 for the 300 μm particle size.

Removal of Cr(VI) from aqueous solutions can be achieved if all five processes are negative.

Abbreviations

FTIR	Fourier Transform Infrared Spectroscopy
EDX	Energy Dispersive X-Ray Analysis
ESR	Electron Spin Resonance
FAAS	Flame Atomic Absorption

Conflicts of Interest

The authors declare no conflicts of interest

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