Valorization of Groundnut Shell Biomass for Biosorption of Hexavalent Chromium from Aqueous Solution

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Abstract

Biosorption is a cost-effective biotechnological innovation for the removal of heavy metals from aqueous solutions. There is widespread research into ways of utilizing agricultural residues to achieve zero waste. Groundnut shells are biodegradable waste available in large quantities. This study investigated the use of groundnut shells for the biosorption of chromium (VI) ions from an aqueous solution. Groundnut shells were cleaned and crushed to make fractions of particle size in the range of 90-1000 μm. The point of zero charge (pH$_{PZC}$) and the distribution of oxygenated acidic and basic surface functional groups were determined. In batch experiments, the effect of acid pre-treatment, initial metal concentration, biosorbent particle size, biosorbent dosage, and contact time on biosorption was investigated. The biomass was found to have a pH$_{PZC}$ value of 6 and was dominated by acidic groups. The best biosorption activity was observed at 20 mg/L initial metal concentration and a biosorbent dosage of 10%. The effect of contact time was dependent on the initial chromium (VI) concentration. At 20 mg/L initial chromium (VI) concentration, the biosorption process reached equilibrium within 60 minutes whilst at high (>80 mg) chromium (VI) concentration equilibrium was not reached, even after 240 minutes. The best biosorption activity was observed with acid-treated biomass of particle size 300 μm. The adsorption fitted best with the Langmuir isotherm model and the pseudo-second-order kinetic model ($R^2 > 0.9982$). Groundnut shell biomass has the potential for the removal of chromium (VI) ions from aqueous solutions and possibly from chromium-polluted effluents on an industrial scale.

Keywords: biosorption, chromium, *Arachis hypogea*, isotherm, biosorbent, kinetics

1. Introduction

Agricultural residues are waste materials available in large quantities after the harvesting of crops. In pursuit of knowledge that promotes ecologically and environmentally friendly practices, new technologies are being developed for the application of agricultural waste in different industries, thereby achieving zero waste production (Duc *et al*., 2019). Groundnuts are mostly grown in Zimbabwe's communal lands. Groundnuts are used in oil and peanut butter production as well as in confectionery and snacks. The world's total production is 50.5 million metric tonnes (USDA-FAS, 2022). Groundnut shells remain as waste after the removal of groundnut seeds and are usually dumped or burned. The shells degrade slowly under natural conditions due to their high lignin content. Burning the shells introduces carbon dioxide and particulate matter into the atmosphere. Burying the shells influences the soil's biological and physico-chemical properties although groundnut shells are not a very good source of compost because of their slow rate of degradation due to the high lignin content (Grandawa, 2014). Groundnut shells have various functional and bioactive properties allowing them to be used as fertilizer, food, briquettes, feedstock, and even in biofilters (Udeh 2018; Patel *et al*., 2017; Lubwama *et al*., 2017; Maruthi *et al*., 2019). Transforming groundnut shells into a valuable product, raw material or ingredient adds value to the shells.

Biosorption is a passive process that is physicochemically and metabolically independent. The pollutants (biosorbate) bind to the surface of the biosorbent (biological carrier material) and are removed from the solution (Zainith *et al*., 2021). The biosorbent is often crushed to fine particle size and then suspended in a solution containing the chemical species to be bound (in this case the metal ion), and incubated for some time until

equilibrium is attained. During the incubation, there is an interaction between the biosorbate and several different functional groups present on the biosorbent surface leading to the passive binding of the two. This binding is often reversible and at times serves the practical purpose to desorb the biosorbate at the end of the process allowing the biosorbent to be re-used. Biosorption makes it possible to selectively bind a metal ion in solution and leave a relatively metal-free effluent to be released into the environment (Chojnacka, 2010).

Biosorption represents a cost-effective biotechnological innovation for removing heavy metals from aqueous solutions. Unlike conventional methods of heavy metal removal, biosorption is highly efficient even at low metal concentrations and has a low energy requirement as the process is passive. Biosorption allows the recovery of metal and repeated use of biosorbent (Rezaei, 2016). Biomass that includes algae, bacteria, fungi, and yeasts as well as agricultural and industrial residues have all been studied as potential biomass materials for metal biosorption. Polar functional groups such as phenolic, amino, alcoholic, and carbonyl, are found on the agricultural waste biomass. The functional groups have a high potential for binding metal ions (Kanamarlapudi *et al*., 2018). Agricultural by-products such as oil palm biomass, soybean shells, potato peels, rice husks, peanut husks, and shells, wheat straw, apricot stone, almond shells, date palm seeds, and corn cobs have been studied and have shown the ability to remove various heavy metals from aqueous solutions (Vakili *et al*., 2014; Witek-Krowiak & Reddy 2013; Aman *et al*., 2008; Kumar & Bandyopadhyay, 2006; Vaughan *et al*., 2001).

Groundnut shells have been used as biosorbent in the removal of heavy metals (such as cadmium, lead, and nickel), drugs, and phenolic compounds (OuYang *et al*., 2014; Shruthi & Pavithra 2018; Cobbina *et al*., 2019; Tatah *et al*., 2017, Tomul *et al*., 2020). In a study by Malik and colleagues, the effect of contact time, adsorbate concentration, and adsorbent dosage were investigated in the biosorption of malachite green dye from aqueous solutions using groundnut shells modified into activated carbon (Malik *et al*., 2007). The study showed that the biosorbent achieved 94.5% removal of the dye in a 30 minutes equilibrium time at a biosorbent dose of 0.5 g/L and an initial dye concentration of 100 mg/L (Malik *et al*., 2007).

Chromium is a known carcinogenic and mutagenic heavy metal. The two most abundant naturally occurring chromium species are the hexavalent [chromium (VI)] and trivalent [chromium (III)] forms (Fernández-López *et al*., 2014). Concentrations higher than 0.05 mg/L for chromium (VI) and 5.0 mg/L for chromium (III) have toxic environmental effects (Labied *et al*., 2018; Rosales *et al*., 2019)). Chromium (III) is relatively non-toxic and is largely water-insoluble. The metal mostly exists as low-solubility hydroxides that are easily adsorbed to soil particles and do not easily permeate biological membranes (Labied *et al*., 2018). In humans, chromium (III) is required as a micronutrient (Quiton *et al*., 2018; Xiao *et al*., 2017). Chromium (VI) is highly soluble in water and permeates biological membranes, causing toxic, mutagenic, and carcinogenic effects (Quiton *et al*., 2018; Xiao *et al*., 2017; Kafilzadeh & Saberifard, 2016; Rezaei, 2016; Shukla *et al*., 2014).

This study aimed to investigate the use of groundnut (*Arachis hypogea*) shell biomass for biosorption of chromium (VI) from aqueous solutions. The biosorption capability of biomass derived from groundnut shells was investigated to determine its potential as a biosorbent for large-scale industrial application.

2. Method

2.1 Preparation of Groundnut Shells

Groundnut shells were collected from the local farm produce market in the city of Bulawayo, Zimbabwe. The shells were washed with distilled water to remove insoluble impurities and dust and air-dried for 7 days at room temperature. Further drying was done in an oven at 105 °C for 24 hours to constant mass. The shells were ground in a blender (Waring® 8010S Laboratory blender) and then sieved using a MACSALAB electronic sieve shaker (Model ES200 Mark IV) to obtain the following particle sizes, 90 µm, 180 µm, 300 µm, 710 µm, and 1000 µm. The ground shell fractions were stored in airtight glass jars in a cool, dry cupboard at room temperature until needed for use.

2.2 Preparation of Solutions and Reagents

A 1000 mg/L stock solution was prepared using analytical-grade potassium dichromate ($K_2Cr_2O_7$) dissolved in distilled water. The stock solution was diluted with distilled water to give chromium concentrations ranging from 20 to 200 mg/L. The acids, that is, 0.1 M hydrochloric acid, 0.1 M nitric acid, and 0.1 M sulphuric acid, were prepared for use in biosorbent treatment as well as the acidification of metal solutions. A 0.25% di-phenyl carbazide (DPC) solution was prepared and acidified using phosphoric acid. The solution was covered with aluminum foil and kept in a dark cupboard to avoid light.

2.3 Biosorbent Characterization

2.3.1 Determination of Biomass Point of Zero Charge (pH$_{PZC}$)

The biomass point of zero charge was determined using the mass titration method (Labied *et al.*, 2018). Exactly 50 mL of a background electrolyte (0.1 M sodium chloride), at different pH values (from 3 to 10), was used per gram of untreated biosorbent in Erlenmeyer flasks. The flasks were shaken (150 rpm) for 48 hours at room temperature. The mixtures were filtered using Whatman No.4 filter paper and the pH of the filtrate was determined. The change in pH was calculated as follows:

$$Change\ in\ pH\ =\ initial\ pH\ –\ final\ pH \tag{1}$$

The point at which the curve of change in pH against initial pH crosses the horizontal axis is the pH$_{PZC}$ point.

2.3.2 Quantification of Surface Oxygen Functional Groups

The Boehm titration method was used to define the oxygen surface functional groups on the groundnut shell biomass surface. Untreated biomass was mixed in Erlenmeyer flasks with different reagents, to define and quantify the various surface oxygen functional groups. A concentration of 0.1 M hydrochloric acid was used to quantify total basic groups, 0.1 M sodium hydroxide for total acidic groups, and 0.05 M sodium carbonate for the quantification of carboxylic, lactonic, and phenolic groups.

The flasks with untreated biosorbent and relevant reagent were shaken at 150 rpm for 48 hours at room temperature. The mixtures were filtered using Whatman filter paper number 4. Exactly 10 ml of solution was placed in flasks and titrated using 0.1 M hydrochloric acid or 0.1 M sodium hydroxide for samples equilibrated in the alkali solutions and hydrochloric acid, respectively. Methyl red was used as a pH indicator. The quantity of the surface oxygen functional groups was then calculated using the back titration calculation method.

2.4 Acid Pre-Treatment of the Biosorbents and Its Effect on Chromium (VI) Biosorption

Crushed and sieved groundnut shell biomass (20 g) was soaked separately in an excess of 0.1 M hydrochloric acid, 0.1 M nitric acid, and 0.1 M sulphuric acid for four hours. After soaking, the acid solutions were drained and the remaining biomass was washed repeatedly in distilled water until neutral pH was reached. A Hanna Digital pH meter Checker® Plus HI98100 (Woonsocket, RI, USA) was used to measure pH throughout the study. The treated biosorbent was dried in an oven at 100 °C for four hours and then stored in an airtight container at room temperature.

To determine the effect of this acid treatment of the biomass on chromium (VI) biosorption and compare the effects of the different acids, each type of treated biosorbent was exposed to 20 mg/L chromium solution at a ratio of 1g/per 50 ml. The flasks were shaken in a shaker incubator at 150 rpm at 25 °C for four hours. All batch experiments were done in triplicates. Aliquots were drawn at 30-minute intervals and the amount of residual chromium at each point was determined using the di-phenyl carbazide (DPC) assay. The performance of the different biomass was expressed in terms of percentage chromium removal and biosorption capacity (Q$_e$) which were determined using the following formulae:

$$Percentage\ Chromium\ (VI)\ Removal\ =\ \frac{Co-Ce}{Co}\ x\ 100 \tag{2}$$

$$Biosorption\ capacity:\ Qe = \frac{Co-Ce}{m} x\ V \tag{3}$$

Where;

C_o is initial Chromium (VI) concentration in mg/L

C is Chromium (VI) concentration at time t

V is volume (L)

m is biosorbent mass (g)

The biosorption capacity (Q$_e$) of a biosorbent, expressed in mg/g of biomass, is the amount of metal ions adsorbed per unit weight of the biosorbent.

2.5 Effect of Initial Metal Concentration on Chromium (VI) Biosorption

To determine the effect of metal concentration on the biosorption of chromium, a series of batch tests were done using the 4 biosorbents (untreated, hydrochloric, nitric, sulphuric acid treated) for adsorption with different initial concentrations of chromium in solution (C$_o$ = 20: 40; 60; 80; 100, 120, 140, 160, 180 and 200 mg/L). Each biosorbent type was mixed with the metal solution at a ratio of 1g to 50 ml and placed in a shaker at 150 rpm for

4 hours at 25 °C. Initial chromium (VI) concentration varied from 20 to 200 mg/L. After incubation and filtration of the solutions, the amount of residual chromium (VI) was determined by the DPC assay. The concentration of the metal that remains in the supernatant at the end of the 4 hours is the equilibrium concentration (C_e).

The amount of chromium adsorbed at equilibrium (Q_e, mg/g) was calculated as follows:

$$Qe = \frac{Co - Ce}{m} x \ V \tag{4}$$

Where;

C_o is initial Chromium (VI) concentration in mg/L

C_e is Chromium (VI) concentration (in mg/L) at equilibrium

V is the volume of the solution (in L), and

m is the mass of the biosorbent (in g).

2.6 Effect of Biosorbent Dosage on Chromium (VI) Biosorption

The effect of the amount of biomass material per batch experiment used was investigated by equilibrating different masses of the biosorbent (0.5-5 g) in an aqueous solution of chromium of concentration 50 mg/L. This resulted in biomass dosage levels in the range of 1-10% (w/v). The mixtures were incubated at 25 °C for 120 minutes with shaking at 150 rpm. After incubation, the mixtures were filtered with Whatman No.4 filter paper and the residual chromium (VI) content in the filtrate was determined using the DPC assay.

2.7 Effect of Biosorbent Particle Size on Chromium (VI) Biosorption

The different biosorbent fractions of different particle sizes were equilibrated in a 20 mg/L solution of chromium (VI) at a ratio of 1 g to 25 ml. The biosorbent particle sizes investigated are 90 μm, 180 μm, 300 μm, 710 μm, and 1000 μm. The mixtures were agitated at 150 rpm at 25 °C for 120 minutes. The mixtures were filtered, and the residual metal ions in each filtrate was analyzed using the DPC assay.

2.8 Adsorption Isotherm Studies

To examine the interaction between biosorbate [chromium (VI)] and biosorbent at equilibrium, two different adsorption isotherm models were applied to the experimental data. Four sets of data were used for modeling. The data was obtained experimentally by a series of batch tests from 4 biosorbents (untreated, hydrochloric acid, nitric acid, sulphuric acid) for the biosorption of chromium in solution with various initial metal concentrations (C_o = 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mg/L). The amount of chromium adsorbed at equilibrium, Q_e (mg/g) was determined as described in section 2.5. The best-fitted model for the adsorption system was determined using the linear forms of the Langmuir (type I) and Freundlich isotherm models. The models are given by the following formulae:

$$\text{Langmuir:} \quad \frac{C_e}{Q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{5}$$

Where: where C_e (mg/L) is the chromium (VI) concentration at equilibrium, Q_e (mg/g) is the amount of chromium (VI) adsorbed per unit mass (1 g) of biomass at equilibrium, q_{max} (mg/g) is the maximum amount of chromium (VI) adsorbed in a monolayer on the biomass, and K_L (L/g) is the Langmuir constant.

$$\text{Freundlich:} \quad ln(Q_e) = ln(K_F) + \frac{1}{n} ln(C_e) \tag{6}$$

Where K_F (mg/g) represents the Freundlich constant, which indicates adsorption capacity.

2.9 Determination of the Adsorption Kinetics

Kinetic studies were carried out using chromium solutions in the concentration range of 20-200 mg/L in increments of 20. Incubation was done at 25 °C for four hours. To obtain the rate of adsorption, the amount of chromium adsorbed was expressed as a function of contact time using Lagergren's pseudo-first-order rate model (Lagergren, 1898), which is a linear plot of ln (Q_e - Q_t) against t (Equation 7). The pseudo-second-order kinetic model, a linear plot of t/Q_t against t (Equation 8), was also used (Ho & McKay, 1998). The linear forms of these models are given by:

$$ln(Q_e - Q_t) = ln(Q_e) - K_1 t \tag{7}$$

$$\frac{t}{Q_t} = \frac{1}{k_2(Q_e)^2} + \left(\frac{1}{Q_e}\right)t \qquad (8)$$

Where;

Q_e is the amount of metal ions adsorbed at equilibrium (mg/g),

Q_t is the amount of metal ions adsorbed at time t, and

K_1 and K_2 are the adsorption rate constants of pseudo-first order and pseudo-second order kinetics, respectively.

3. Results and Discussion

3.1 Point of Zero Charge (pH_PZC) Determination

The pH$_{PZC}$ for the untreated groundnut shell was pH 6 (Figure 1). Properties of biosorbents and adsorbates such as ionic state are influenced by pH. Depending on the charge of the polluting molecule, the magnitude of the pH$_{PZC}$ determines whether the biomass should be acid or alkali-treated. Chromium (VI) in an aqueous solution exists predominantly in the anionic state. This implies that for maximum adsorption, the biosorbent should, by nature or upon modification, be largely positively charged. In the current case, the biomass has a very high point of zero charge (pH 6). To shift the equilibrium of charges on the biomass towards a more cationic nature, it is necessary to treat the biomass with acids as well as to perform the experiments at acidic pH. The pH used in the batch experiments for this study was 3.5 (less than the pH$_{PZC}$).
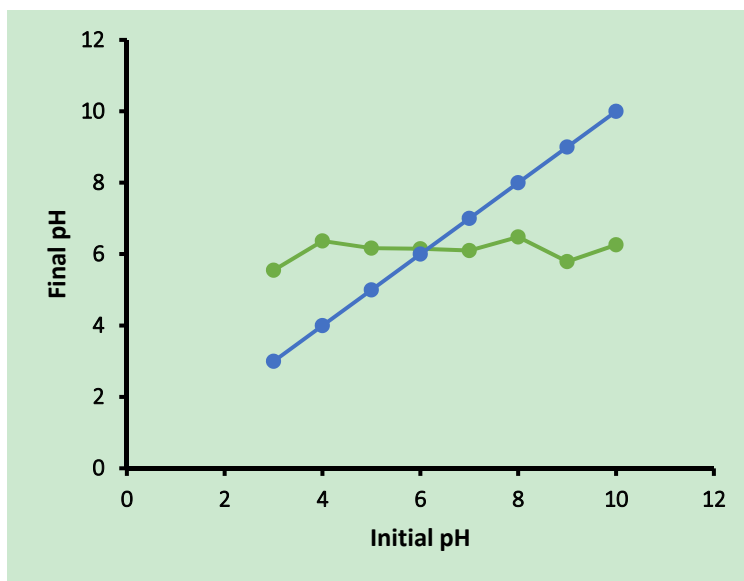

Figure 1. Point of zero charge (pH$_{PZC}$) determination for Untreated Groundnut shell biomass tested at pH values ranging from 3 to 10

3.2 Distribution of Oxygenated Acidic and Basic Surface Functional Groups

The distribution of different acidic and basic functional groups on the biomass surface was investigated using the Boehm titration method and the results are shown in Table 1.

Table 1. Relative quantities of basic and acidic functional groups on the groundnut shell biomass

Functional group	Quantity (mmol/g)
Acidic groups	
Phenolic	0.442
Lactonic	0.181
Carboxylic	4.356
Total acidic groups	4.979
Total basic groups	1.121

The surfaces of the groundnut shells were dominated by acidic groups (Table 2). Of the three acids assayed for, carboxylic acids appeared to dominate, followed by phenolic acids and lastly lactonic acids. This dominance of acidic groups is ideal for the removal of Cr^{6+} ions from solution through physical adsorption and ion exchange (Kanamarlapudi *et al.*, 2018).

3.3 Effect of Biosorbent Pre-Treatment on Biosorption Performance

Having determined that the groundnut shell biomass has a high point of zero charge and the biosorbate of interest is cationic in solution, the biosorbent was subjected to treatment by three different acids namely hydrochloric, sulphuric, and nitric acid before use.
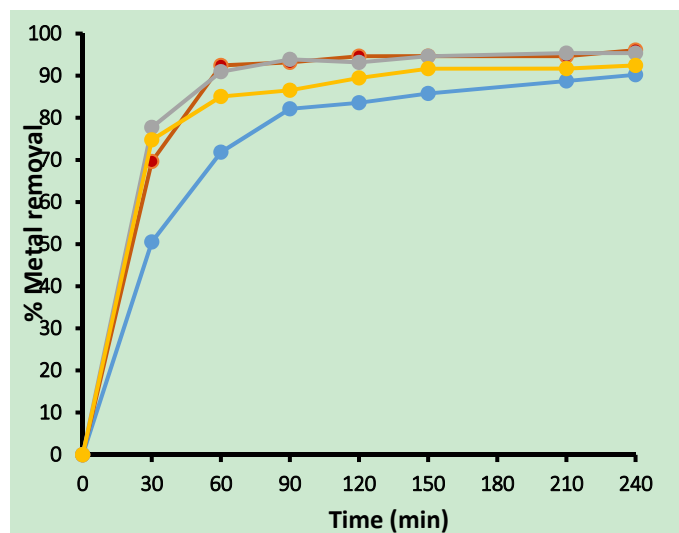

Figure 2. Effect of untreated (●), hydrochloric acid (●), nitric acid (●), and sulphuric acid (●) treatments on biosorbent performance at an initial chromium (VI) concentration of 20 mg/L, pH 3.5 and 25 °C, over a contact time of 4 hours

All three treatments as well as the control (untreated biomass) produced a similar trend where chromium (VI) removal was highest in the first 25 to 30 minutes. The three acids used to pre-treat the biomass appeared to produce similar results in biosorption. The use of dilute acid hydrolyses surface polymers and increases porosity, thus increasing the surface area for adsorption Akhabue *et al.*, 2019). Sulphuric acid is cheaper compared to nitric and hydrochloric acid; therefore, it is widely used in industry (Chen *et al.*, 2012). The effect of acid treatment on biosorption capacity (Q_e) was also determined and the results are presented in Table 3.

Table 3. Effect of acid treatment on absorption capacity (Q_e)

Biomass treatment	Biosorption capacity Q_e (mg/g)
Untreated	0.90
Hydrochloric acid-treated	0.96
Nitric acid-treated	0.95
Sulphuric acid-treated	0.92

From the results, it is implied that a gram of hydrochloric acid-treated biomass removed 96% of the available chromium (VI) ions. Chemical modification of the biomass is known to increase the interaction of the positively charged biomass and the largely anionic chromate ions. Despite the untreated biomass showing considerable biosorption activity, the acid treatment appears to have improved the performance of the biosorbent by up to 6% (Figure 2). The use of acid treatment enhances the performance of a biosorbent. Since acid pre-treatment hydrolyses the cellulose and hemicellulose into its monomers it, therefore, enhances the availability of functional groups and produces a biosorbent with high microporosity.

3.4 Effect of Initial Metal Concentration on Chromium (VI) Adsorption
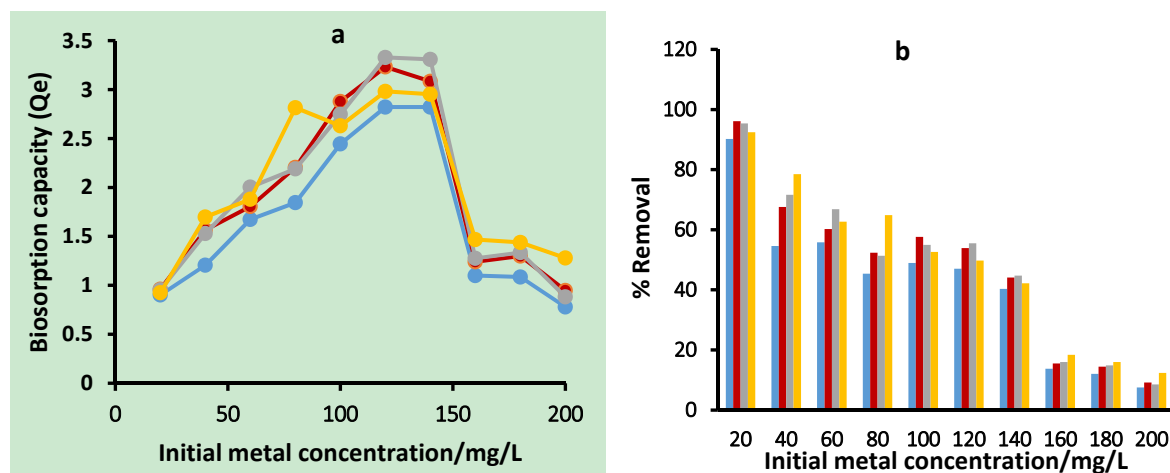

Figure 3. Effect of initial metal concentration on chromium (VI) removal with untreated (●), hydrochloric acid (●), nitric acid (●), and sulphuric acid (●) -treated biomass at pH 3.5, and 25°C, over a contact time of 4 hours, presented as biosorption capacity (a) and percentage removal (b)

Chromium removal from aqueous solution was highest (96% removal) at a low initial metal concentration of 20 mg/L and declined gradually with increasing initial metal concentration (Figure 3). The high biosorption activity observed demonstrates the potential of biosorption as a viable method for the removal of chromium (VI) ions from aqueous solutions with low metal levels using small quantities of biomass material. Other pollutant removal methods such as chemical adsorption show reduced efficiency at low pollutant levels; hence biosorption becomes a suitable alternative.

As initial metal concentration (C_0) was increased from 20-120 mg/L, the biosorption capacity of the modified groundnut shells (Q_e) increased roughly linearly, although the percentage of chromium removal decreased (Figure 3). Further increase in initial metal concentration beyond 120 mg/L caused a decrease in Q_e. The mechanism of the metal uptake generally depends on the initial concentration of heavy metals in contact with the adsorbent (Rao & Kashifuddin 2014). The initial metal concentration is the force that surmounts any mass transfer barriers limiting the transfer of the metal ions from the liquid phase to the solid phase. However, beyond certain levels, the amount of binding sites available becomes limiting. The increased amount of metal bound to the biosorbent at higher metal levels demonstrates that the low Q_e values observed at low initial metal concentration were due to a mismatch between available binding sites and available adsorbate.

The findings of this study demonstrate that the adsorption of chromium (VI) ions onto groundnut shell-based biomass is most rapid with an excess of binding sites and gradually slows down as the proportion of binding sites declines. This is similar to the trends observed by other researchers who discovered that most adsorption occurred in the first 35 minutes of exposure of the biosorbent to industrial effluent (Sreedhar & Reddy 2019; Ahamad *et al.*, 2019). At low metal ion loads, adsorption involves high-energy sites. In such conditions, the proportion of metal ions to available adsorption sites is low, thus increasing the amount adsorbed per unit mass (Brodeur, et al., 2011). As such, more chromium ions are left in solution at higher concentrations due to the saturation of binding sites. This suggests the involvement of energetically less favorable sites with increasing metal ion concentrations. The adsorption capacity increases due to the high chance of interaction between the metal ions and the groundnut shell at high metal concentrations (Bayou *et al.*, 2019; Ghaffari *et al.*, 2014). The mass transfer resistance of the metal ion is overcome by the high concentration gradient provided by higher initial concentration levels. The higher energy sites are rapidly saturated and the metal ions gradually occupy the lower energy sites, resulting in a continuous increase in the amount adsorbed per unit mass, albeit with a reduction in binding rate (Hubbe *et al.*, 2019).

3.5 Effect of Biosorbent Dosage on Chromium (VI) Biosorption

The effect of varying biosorbent dosage on chromium (VI) biosorption and biosorption capacity is shown in Figure 4 (a) and Figure 4 (b) respectively.
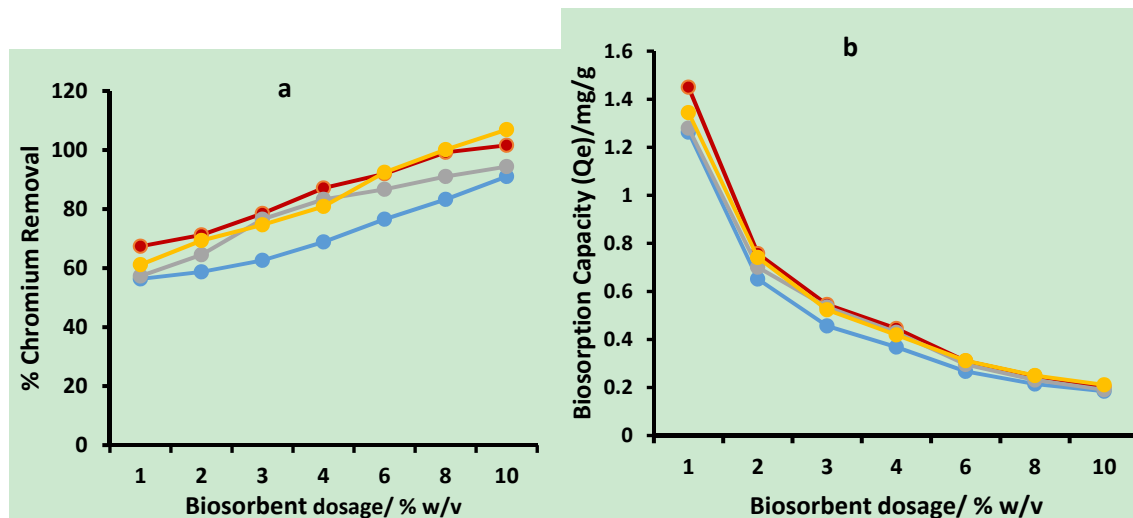
Figure 4. Effect of biosorbent dosage on chromium (IV) biosorption in untreated (●), hydrochloric acid (●), nitric acid (●), and sulphuric acid (●) treatment at pH 3.5, temperature 25 °C and initial metal concentration 20 mg/L over, 120 minutes presented as percentage chromium removal (a) and biosorption capacity (b)

Increasing the biosorbent dose resulted in increased metal removal. At 1% biosorbent dosage, the average chromium removal was 60.57% whilst total removal of the metal was achieved at 8% dosage using acid-treated biosorbent. This is most likely due to the availability of more adsorption sites with the increased dosage (Labied *et al*., 2018; Fernández-López *et al*., 2014; Stjepanovic *et al*., 2021). At 10% (w/v) biosorbent level, near total elimination of the metal was observed in all treated biosorbents. This increase in biosorption coincided with a reduction in biosorption capacity (Q_e). Higher Q_e values (1.26 -1.45 mg/g at 1% dosage) were obtained with reduced amounts of biosorbent in solution. As biosorbent dosage was increased, there was a rapid decline in the amount of metal ions adsorbed per unit mass of biosorbent, as shown by the lower Q_e values (0.18–0.21 mg/g at 10% dosage). This suggests that there may be an interaction between biosorbent particles leading to the formation of biosorbent aggregates which in turn reduces the total surface area and hence the number of available sorption sites (Kiran *et al*., 2013). Some of the adsorption sites remain unsaturated during the adsorption process.

3.6 Effect of Biosorbent Particle Size on Chromium (VI) Biosorption

Biosorbent particle sizes ranging from 90-1000 μm were tested with an initial metal concentration of 20 mg/L and the effect on biosorption capacity (Figure 5).
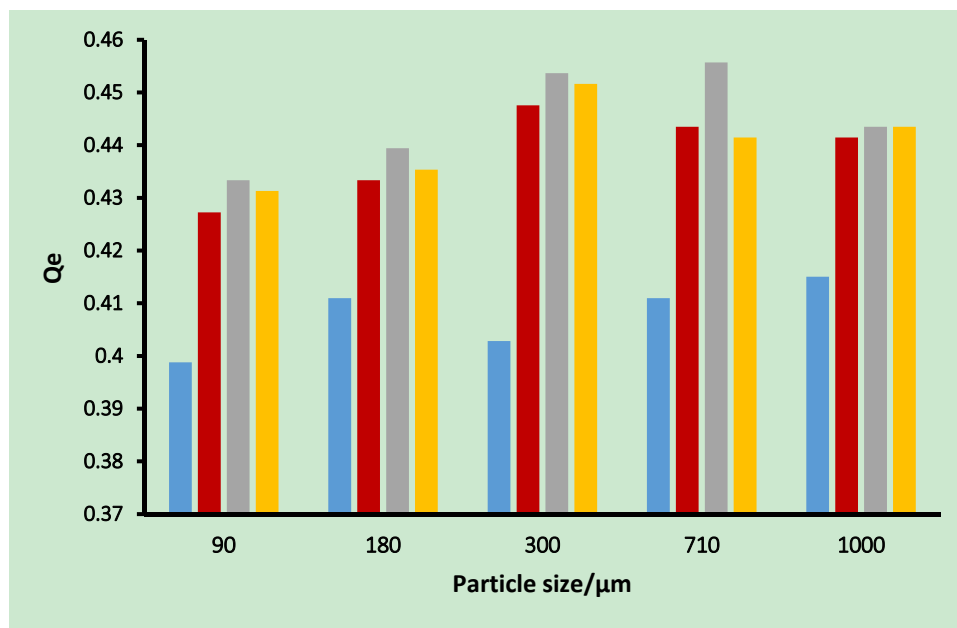
Figure 5. Effect of particle size in untreated (•), hydrochloric acid (•), nitric acid (•), and sulphuric acid (•) treated biosorbent on chromium (IV) biosorption at an initial metal concentration of 20 mg/L, at 25 °C, over a contact time of 120 minutes

The best biosorption activity was observed with the 300 μm biomass size fraction. In general, smaller particle sizes present a much larger surface area for biosorption to occur whereas larger particle size fractions present a reduced surface area for adsorption to take place at the same biosorbent dosage (Mishra *et al*., 2015). However, agglomeration of small-sized particles may occur thus reducing the available surface area for biosorption. This explains the lower chromium (VI) removal by the 90 μm biomass. Larger particles (300 -1000 μm) produced a clear filtrate, unlike the smaller biomass particle sizes which produced a murky filtrate. It is thus ideal to use a larger particle size where its biosorption efficiency is comparable to that of smaller particle size biomass.

3.7 Adsorption Isotherms

The equilibrium data were applied to the Langmuir and Freundlich isotherm models, and the model with the best fit was determined using the results of their linear regressions. All biosorbent treatments showed high correlation coefficient (R^2) values for the Langmuir isotherm, with an average of 0.89 (Table 4). Sulphuric acid-treated biomass produced the highest correlation coefficient of 0.98, followed by nitric and hydrochloric acid-treated biomass both with correlation coefficients of 0.89. Untreated biomass gave a correlation coefficient of 0.81. The correlation coefficients shown in all treatments to the Langmuir isotherm model are high, suggesting that the Langmuir isotherm model adequately describes the biosorption of chromium (VI) ions onto untreated and acid-treated groundnut shell biomass.

Table 4. Langmuir and Freundlich isotherm parameters obtained by linear fitting for the four biosorbents

Biosorbent treatment	Langmuir isotherm			Freundlich isotherm		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	$Kf(mg/g)(mg/l)^{-1/n}$	N	R^2
Untreated	3.2992	0.04617	0.8107	1.1005	3.9888	0.0139
Hydrochloric acid	3.5855	0.06871	0.8851	1.1395	2.8637	0.0376
Nitric acid	3.5881	0.07908	0.8911	1.1363	2.7397	0.0324
Sulphuric acid	3.2404	0.1226	0.9772	1.2232	3.2765	0.0998

According to the Langmuir adsorption isotherm model, it can be concluded that chromium (VI) ions are adsorbed reversibly in a monolayer onto a fixed number of homogenous binding sites on groundnut shell-derived biomass. The Langmuir adsorption model assumes maximum surface coverage at high metal concentrations and linear

adsorption at low densities. The R^2 values lie between 0 and 1, confirming the favourability of the adsorption processes under the investigated conditions (initial metal concentration 20 mg/L, temperature 25 °C, pH 3.5). The monolayer adsorption capacity (q_m) values are 3.30 (untreated), 3.59 (hydrochloric acid), 3.59 (nitric acid), and 3.24 (sulphuric acid) mg/g showing the high biosorption capacity of the groundnut shells. The values of the Langmuir constant K_L (0.05 (untreated), 0.07 (hydrochloric acid), 0.08 (nitric acid), and 0.12 L/mg (sulphuric acid)) are relatively high. This implies high bonding between the chromium (VI) ions and the groundnut shell as a result of the high surface energy in the process.

3.8 Effect of Contact Time and Adsorption Kinetics

At 20 mg/L initial metal concentration, equilibrium was reached after 60 minutes whilst at a high metal concentration (>100 mg/L), equilibrium was not reached even after 240 minutes incubation. Depending on system requirements, it is often important to design a system that allows for the removal of contaminants in the shortest possible amount of time. The results obtained show that adsorption from a low initial metal (20 mg/L) medium occurred in three distinct phases (Figure 2). The highest rate of metal removal occurred in the first 30 minutes of the process possibly due to the high concentration gradient between the metal ions in the solution and the number of unoccupied sites on the biosorbent surface as observed by Chigondo and Nyamunda (2013) when they used baobab fruit shell biomass as adsorbent for the biosorption of lead (II) and copper (II) ions from aqueous solution.

The kinetics of the biosorption of chromium (VI) ions onto untreated and acid-treated groundnut shell biomass rate was analyzed using the pseudo-first-order and pseudo-second-order models. Table 5 shows the parameters for the pseudo-first-order and pseudo-second-order models for the experimental data.

Table 5. Parameters of the pseudo-first order and pseudo-second order kinetic models for the adsorption of chromium (VI) onto groundnut shell biomass

Treatment	First-order kinetic model			Second-order kinetic model		
	K_1(min-1) X 10^{-4}	q_e(mg/g)	R^2	K_2(g/mg/min) X 10^{-4}	q_e(mg/g)	R^2
Untreated	172.058	0.5549	0.9313	406.5	24.676	0.9985
Hydrochloric acid	223.4	0.2697	0.7974	1317.3	7.655	0.9986
Nitric acid	234.9	0.2356	0.8488	1868.6	5.465	0.9997
Sulphuric acid	262.5	0.601	0.8648	836.5	12.292	0.9982

The correlation coefficient R^2 shows the conformity between the experimental data and the model predicted values. The pseudo-first-order model gave relatively low correlation coefficients (average R^2 = 0.861) (Table 5) when compared with the pseudo-second-order kinetic model (average R^2 = 0.999). This shows that the adsorption of chromium ions onto groundnut shells follows the pseudo-second-order kinetic model. This implies that the rate of chromium uptake by groundnut shell biomass slows down based on the filling of adsorption sites (Hubbe *et al.*, 2019). Similar findings were reported by Labied and colleagues while investigating the biosorption of chromium (VI) onto *Ziziphus jujuba* cores processed into activated carbon (Labied *et al*. 2018). Biosorption rates determine the success of potential scale-up and implementation of prospective systems to remove pollutants from water.

4. Conclusions

The groundnut shell biomass removed large quantities of the metal from the aqueous solution even with minimal physical or chemical pre-treatment. It was demonstrated that the efficiency of biosorption of chromium depends on initial metal concentration, biosorbent dose, and contact time. Chromium removal increased with a decrease in initial metal concentration and an increase in dosage of the biosorbent. The optimum chromium (VI) removal was attained with an initial metal concentration of 20 mg/L using an acid-treated biosorbent at a dosage of 2% (w/v), and a contact time of 60 minutes. This confirms that chromium can be removed efficiently using small quantities of biosorbent. Dilute acid pre-treatment was found to be effective in improving the biosorption capacity of the groundnut shells, resulting in 95% chromium removal with an initial metal concentration of 20 mg/L and a contact time of 60 minutes. Untreated biomass achieved 80% chromium removal with an initial metal concentration of 20 mg/L and contact time of 150 minutes. This shows that ground untreated biomass can be used just as well to remove chromium (VI) from aqueous solutions in situations where time is not critical.

The biosorption of chromium (VI) onto groundnut shell biomass follows the Langmuir isotherm, with a maximum monolayer adsorption capacity, q_{max} in mg of chromium (VI) per g of biomass, of 3.30 (untreated), 3.59

(hydrochloric acid), 3.59 (nitric acid) and 3.24 (sulphuric acid). The kinetic data best fits the pseudo-second-order model. These results lay a solid foundation for the harnessing of this technology in the industrial-scale treatment of metal-containing industrial effluent. Agricultural waste is abundant, reusable, low cost and environmentally benign and thus is very attractive for use in the treatment of industrial effluent at a large scale.

Acknowledgments

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