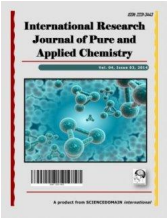


*International Research Journal of Pure & Applied Chemistry*

*18(3): 1-14, 2019; Article no.IRJPAC.9352*
*ISSN: 2231-3443, NLM ID: 101647669*

# Biosorption Studies of Cr(VI) Ion from Aqueous Solution using Unmodified and Oxalic Acid Modified African Yam Bean Pod and Groundnut Shell

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***Authors' contributions***

*This work was carried out in collaboration with all authors. Author SAO designed the study and wrote the protocol. Author HNE preformed the analyses of the study, managed the literature search and wrote the first draft of the manuscript with assistance from author CUS. All authors read and approved the final manuscript.*

***Article Information***

DOI: 10.9734/IRJPAC/2019/v18i330091
Editor(s):
(1) Wenzhong Shen, State Key Laboratory of Coal Conversion Institute of Coal Chemistry, CAS, China.
Reviewers:
(1) Haq Nawaz Bhatti, University of Agriculture Faisalabad, Pakistan.
(2) Lovell Agwaramgbo, Dillard University, USA.
(3) Mulu Berhe Desta, Mekelle University, Ethiopia.
(4) Tariq S. Najim, University of Mustansiriya, Iraq.
Complete Peer review History: http://www.sdiarticle3.com/review-history/9352

***Original Research Article***

***Received 12 August 2014***
***Accepted 10 November 2014***
***Published 12 April 2019***

## ABSTRACT

This study examines the removal of $Cr^{6+}$ from aqueous solutions using unmodified and oxalic acid modified African yam bean (AYB) pod and groundnut (G'NUT) shell as adsorbents. The effects of time, pH, temperature, and metal ion concentration were investigated. The amount of metal ions adsorbed increased as the initial concentration increased; groundnut shell gave a better adsorption capacity. Maximum uptake was recorded at pH of 6.0 whereas uptake level decreased at pH greater than 6.0. Kinetic studies showed that the physisorption reaction rates could be described better by a pseudo-second order model with $R^2$ values close to 1. Various thermodynamic parameters such as $\Delta G^o$, $\Delta S^o$, and $\Delta H^o$ were calculated. The values obtained for $\Delta G^o$ were all negative for both adsorbents; indicating that the sorption processes investigated was spontaneous. Findings showed

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that an increase in temperature results in a lower metal loading per unit weight of the adsorbents, suggesting exothermic nature of the process. The process was also examined in terms of Freundlich adsorption model which showed $R^2$ values between 0.6952 and 0.9956. From the parameters considered, it was revealed that the modification of the adsorbents with oxalic acid enhanced their adsorption capacity.

*Keywords: Adsorption; African yam bean pod; groundnut shell; chromium (VI); kinetics; thermodynamics; isotherm studies.*

## 1. INTRODUCTION

The process of heavy metal removal by biological material is called biosorption. Biosorption can also be described as a process in which solids of natural origin are employed for binding heavy metals [1]. It can mainly be used for treatment of wastewater with low or medium initial heavy metal concentration. However, enhanced industrial activities during recent decades have led to the discharge of unprecedented volumes of water which is a serious cause of environmental degradation. Heavy metals due to their high toxicity, pose a serious threat to biota and the environment [2]. Therefore, it is necessary to alleviate these metals from industrial effluents before their discharge into water bodies. In recent years, biosorption has been recognised as an effective method of deduction of metal contamination in surface water and in industrial effluents [3].

Cr(VI) is an example of some heavy metals with detrimental effects on human, plants and animals. Chromium exists in nine valence states ranging from -2 to +6. From these, only the hexavalent [Cr(VI)] and trivalent chromium [Cr(III)] have primary environmental significance since they are the most stable oxidized forms in the environment [4]. Both are found in various bodies of water and wastewaters. Chromium also occurs more frequently as Cr(VI) and Cr(III) in aqueous solutions [5]. Cr(VI) typically exists in one of these two forms: chromate ($CrO_4^{-2}$) or dichromate ($Cr_2O_7^{2-}$), depending on the pH of the solution [6]. These two divalent oxyanions are very water soluble and poorly adsorbed by soil and organic matter, making them mobile in groundwater [4]. Both chromate anions represent acute and chronic risks to animals and human health, since they are extremely toxic, mutagenic, carcinogenic and teratogenic [7]. The toxicity of this heavy metal to marine life and consequently to man has been established for many years.

However, the chemistry of this heavy metal is complex and interesting especially when it finds its way into human metabolism. Both valences of chromium pose a greater risk due to their carcinogenic properties [5]. Although Cr(III) is less toxic than Cr(VI), a long term exposure to trivalent chromium is known to cause allergic skin reactions and cancer [8, 1]. On the other hand, $Cr^{6+}$ causes skin irritation or ulceration due to acute exposures at above maximum contaminant level (MCL) [9]. It also causes damage to liver, kidney circulatory and nerve tissues; dermatitis as well as cancer on prolonged exposure. Strong exposure of Cr(VI) causes cancer in digestive tract and lungs and may cause epigastria pain, nausea, vomiting, severe diarrhoea and haemorrhage [10]. Nonetheless, biological membranes are said to be impermeable to Cr(III) but Cr(VI) can penetrate through and may be reduced in the mitochondria, nuclei and cytoplasm to Cr(III) which readily forms insoluble chromium hydroxides at pH 7.5 [11]. It is noteworthy to mention that the guideline value of Cr as an inorganic constituent of health significance is 0.05 mg/L. According to Environmental Protection Agency (EPA), the permissible level for Cr(III) and Cr(VI) in drinking water is 0.1 mg/L [11].

Chromium and its compounds are widely used in electroplating, leather, tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile, steel fabrication and canning industries [10]. These industries produce large quantities of toxic wastewater effluents. It is therefore essential to remove chromium from wastewater before disposal [10]. Several methods exist for removal of heavy metal pollutants from liquid wastes where they are present in high concentrations. These include methods such as precipitation, electroplating, ion exchange and membrane processes [12]. Currently, chemical precipitation is most widely used for the treatment of chromium-bearing effluents [1]. In fact, these processes are difficult to implement on large scale due to expensiveness and other limitations such as ineffectiveness at low concentrations

(< 100 mg/L) and production of toxic sludge and /or other waste products that also need disposal [12,13].

In this regard, low cost biosorbents such as seaweeds, moulds, yeasts, bacteria, crab shells, agricultural products such as wool, rice straw, coconut husks, peat moss, cocoa pod husk [14, 15], exhausted coffee [16], maize cob and husk [17-19], sunflower stalk [20], chitosan and N-carboxymethyl chitosan [21,22]; bacteria, algae [23,24] and so on, have been tested and proven good. However, the literature is still insufficient to cover this problem and more work and investigations are needed to deal with other locally available and cheap adsorbents to eliminate Cr(VI) from industrial composition. In the present study, sorption of Cr(VI) ion onto unmodified and oxalic acid modified African yam bean pod (AYB) and groundnut shell (G'NUT) was studied. The effects of pH, temperature, time, initial metal ion concentration were studied. Freundlich adsorption isotherm model was applied along with sorption kinetics and thermodynamic study to elucidate the experimental data.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Biomass (biosorbents)

African yam bean pod used was obtained from Arochukwu, a town in Abia State, Nigeria while the groundnut shell was obtained from a local market in Owerri, Imo State, Nigeria. The shells and pods of these legumes were removed, crushed in a mill and washed separately with deionised water and air dried. The material samples were sieved through 1000 µm mesh size first and then through 850 µm, 450 µm and 250 µm mesh sizes. However, the samples retained on 250 µm mesh size were most abundant for the two biosorbents on sieve-screening and were further used for the entire biosorption study. They were separately soaked in dilute nitric acid solution (2 % v/v) for 24 hr to remove any debris or soluble biomolecules that might interact with metal ions followed by washing with deionised water and oven drying for 6 hr at 105°C. Each of the samples was divided into two parts and one part was taken for modification.

#### 2.1.1 Modification of biosorbents with oxalic acid

The treated G'NUT shell and AYB pod samples were taken for modification with oxalic acid to create more surface area and incorporate more hydroxyl group necessary for bonding and to make sure that organic matter content is reduced tremendously. Specifically, they were soaked in 3 M $(COOH)_2$ for 24 hr and rinsed severally with deionised water until a pH of 6.5 was achieved. The remaining biomasses after the rinsing were oven dried at 105°C for 24 hr and stored in separate air-tight containers.

Oxalic acid is a relatively strong acid despite being a carboxylic acid. It is also a reducing agent [25] and its conjugate base, oxalate ($C_2O_4^{2-}$), is an excellent ligand and a chelating agent for metal ions and cations [26]. However, the oxalic acid modification of the biosorbents led to the carboxylation of the biomass with the displacement of the hydroxyl groups of the biomass by the oxalate groups, as illustrated by the following reaction:

$$\text{Biomass–2OH} + H_2C_2O_4 \rightarrow \text{Biomass–}C_2O_4^{2-} + 2H_2O \quad \ldots (1)$$

### 2.2 Preparation of Stock Solutions

All chemicals and reagents used for the experiment and analysis were of analytical grade. Stock solution of 1000 mg/L of Cr(VI) ion was prepared by dissolving 1 g of $CrO_3$ in 1 L of deionised water. Various aliquots were obtained into 100 mL volumetric flask and made up to mark with deionised water to give a range of concentrations between 20 mg/L and 100 mg/L. The pH of the solutions was adjusted to 6.5 using 0.1 M HCl or NaOH. Fresh dilutions were made for each study.

### 2.3 Equilibrium Sorption of Metal Ions on Biomass Materials

The biosorption capacity of AYB pod and G'NUT shell was determined by contacting various concentrations (20 – 100 mg/L) in 250 mL Erlenmeyer flasks containing 1 g of biosorbent; corked and shaken in a rotary shaker at 120 rpm. After 1 hr, the contents of the flasks were filtered and the equilibrium concentrations determined by using atomic absorption spectrophotometer (UNICAM Solar 969 model). For the determination of rate of biosorption on both metal ions from 100 mg/L, the supernatant were analysed for residual Cr(VI) after the contact period of 10, 30, 60, 90, 120 min. The effect of pH was determined at pH values of 2, 4, 6, 8 and 10 while temperature of 273 K, 293 K and 303 K were used to study the effect of temperature. Initial metal ion concentrations of 20, 40, 60, 80

and 100 mg/L were used for the effect of concentration while maintaining adsorbent dosage of 1 g / 100 mL volume of solution.

The amount of metal ions adsorbed by the biosorbent was determined using a mass balance equation expressed as:

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

where $q_e$ is the amount of metal ion adsorbed (mg/g) by the biosorbent at equilibrium, $C_o$ is the initial concentration of metal ion in the solution (mg/L), $C_e$ is the equilibrium concentration or final concentration of metal ion in the solution (mg/L), V is the volume of initial metal ion solution used (mL), m is the mass of the biosorbent (g). To minimize error, the mean value of the triplicate values for each case was used for calculation.

The percent biosorption (%) was also calculated using the equation:

$$\%\,\text{biosorption} = \frac{C_o - C_e}{C_o} \times 100 \quad (3)$$

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of pH

The solution pH has been reported to be one of the most important variables governing the biosorption of metal ions by biosorbents [27]; as metal adsorption can dramatically change with change in pH accordingly. For obtaining the optimum pH for metal ion biosorption by modified and unmodified AYB pod and G'NUT shell, the removal of Cr(VI) ion from their aqueous solutions were studied at different pH values as shown in Fig. 1. From the graph, the percent adsorbed of $Cr^{6+}$ removed increased from pH 2.0 to 6.0 and hence showed some decline thereafter (i.e. from pH 6.0 to 10) for the modified adsorbents. The highest uptake level of 99.86 % was recorded for $Cr^{6+}$ on groundnut shell by the modified biosorbents. The removal of metals from aqueous solutions by adsorption is related to the pH of the solution, since pH affects the surface charge of the adsorbent degree of ionization. It was observed that biosorption was lowest at initial pH 2.0 and increased progressively as the pH increased and then began to drop; further increase in pH was insignificant as the optimum biosorption for the metal ion was reached at pH 6.0 for both biosorbents in the modified medium, while in the unmodified medium, biosorption rate increased progressively with pH until at pH 8.0, it began to tail. The increase in metal removal as the pH increases can be explained on the basis of decrease in competing proton and metal cations for the same functional group and by the decrease in the positive surface charge resulting in a lower electrostatic repulsion between the surface and the metal ion. Similar observation was noted by [28, 29]. The decrease at high pH may be attributed to the decrease in solubility of metals at high pH. Arpa et al. [30] pointed out that there is the tendency for hydrolysis because of higher charge size. However, modification did not have much effect with this parameter.

### 3.2 Effect of temperature

Temperature has an influence on the biosorption of metal ions, but to a limited extent under a certain range, which indicates that ion exchange mechanism exists to some extent. From Fig. 2, adsorption was highest at 303 K for the two adsorbents and continued to decrease as the temperature increases. The maximum equilibrium capacity for Cr(VI) ion by AYB pod and groundnut shell was reached at that temperature for the modified biosorbents. This decrease in biosorptive capacity at higher temperature may be due to the damage of the active binding sites in the biomass [31] and the weakening of the attractive forces between biomass surface and metal ions [32]. The equilibrium capacity of the unmodified AYB pod increased with increase in temperature but later decreased at higher temperature; the increase according to [33], is the increase affinity of sites for metal or binding sites at certain range of temperature. However, modification increased the uptake level of Cr(VI) ion for both biosorbents with preference to groundnut shell.

From results obtained, adsorption of Cr(VI) ion tend to decrease with increase in temperature indicating that a physical adsorption mechanism is favoured. For a physical adsorption mechanism, the extent of adsorption tends to decrease with increase in temperature.

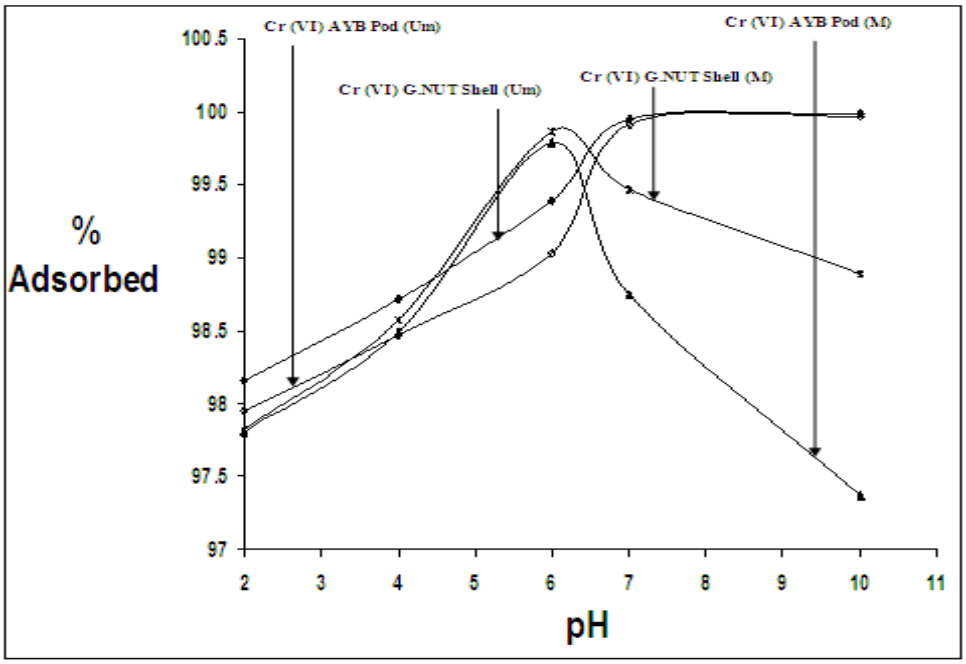


**Fig. 1. Variation of pH for adsorption of Cr(VI) using modified and unmodified AYB Pod and G.NUT Shell**

### 3.3 Thermodynamic study

However, the effect of temperature on biosorption depends on the enthalpy change. Therefore, the biosorption equilibrium constant, $k_d$, is described thermodynamically by Van't Hoff equation as:

$$\ln k_d = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

The values of Gibbs free energy can be calculated by using the following equation:

$$\Delta G = -RT \ln k_d \quad (5)$$

where ΔH, ΔS and ΔG are the changes in enthalpy, entropy and Gibbs free energy of the system respectively. T is the absolute temperature (K), R is the gas constant and $k_d$ is the equilibrium constant given by the equation below:

$$k_d = \frac{q_e}{C_e} \quad (6)$$

Values of $k_d$ ($Lg^{-1}$) were calculated at different temperatures using the above equation, where $q_e$ and $C_e$ are the amounts of the metal ions adsorbed at the various temperatures and the equilibrium concentrations of the metal ions for the various temperatures studied respectively. The plot of the reciprocal of temperature (1/T) versus ln $k_d$, yielded straight lines from where ΔH and ΔS were determined from the slope and intercept of lines (not shown). The values of ΔG at different temperatures were calculated and are listed in Table 1.

**Table 1. Thermodynamic parameters of African yam bean pod and groundnut shell onto $Cr^{6+}$ at varied temperatures**

| Metal Ion | African yam bean pod (Unmodified) | | | | | African yam bean pod (Modified) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ΔH | ΔS | ΔG (kJ/mol) | | | ΔH | ΔS | ΔG (kJ/mol) | | |
| | (kJ/mol) | (J/mol/K) | 303 K | 323 K | 343 K | (kJ/mol) | (J/mol/K) | 303 K | 323 K | 343 K |
| $Cr^{6+}$ | 7.16 | 51.20 | -8.35 | -9.38 | -10.40 | -8.27 | 7.24 | -10.47 | -10.61 | -10.76 |
| | Groundnut shell (Unmodified) | | | | | Groundnut shell (Modified) | | | | |
| $Cr^{6+}$ | 15.07 | 74.84 | -7.60 | -9.10 | -10.60 | -24.08 | -38.66 | -12.36 | -11.59 | -10.82 |

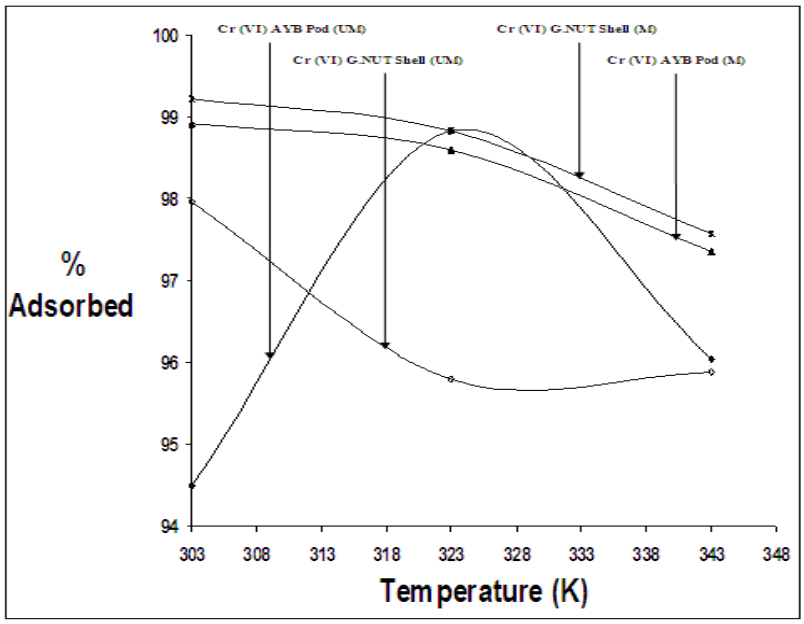


**Fig. 2. Variation of temperature for adsorption of Cr(VI) using modified and unmodified AYB Pod and G'NUT Shell**

From the table, we could see that the thermodynamic treatment of the sorption data indicated that $\Delta G^o$ values were negative for both modified and unmodified biosorbents. The negative values of $\Delta G^o$ indicate the spontaneous nature of adsorption of the Cr(VI) ions by the biomass [32].

It has been reported that $\Delta G^o$ up to –20 KJ/g/mol are consistent with electrostatic interaction between sorption sites and the metal ions (physical adsorption), while $\Delta G^o$ value more negative than –40 KJ/mol involved charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) [34]. The $\Delta G^o$ values obtained in this study for the two metal ions were > –12.36 KJ/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process.

The negative value of $\Delta H$ on the modified biosorbents suggests the exothermic nature of biosorption. $\Delta S$ was almost negative in the modified medium; this confirms the decreased randomness at the solid solution interface during biosorption while positive values of $\Delta S$ seen among the unmodified adsorbents show that the freedom of the metal ions are not too restricted in the biomass, thus confirming a physical adsorption.

### 3.4 Effect of Contact Time

The results of biosorption at different shaking time are illustrated in Fig. 3. From the graph, the uptake of metal ions increased quickly on both adsorbents and after 10 min, the change became slow. The slower phase lasted for the next 30 to 60 min. Adsorption was speedy in the first 10 min of sorption process to the extent that biosorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed metal ion did not significantly change with time. In the two-stage sorption, the first is rapid and predominant and the second slower and quantitatively insignificant [35]. The rapid stage is probably due to the abundant availability of active binding sites at the very early stage of contact and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage. This is obtainable for both modified and unmodified biosorbents.

### 3.5 Sorption Kinetics

In order to analyse the biosorption kinetics of heavy Cr(VI) ion, the pseudo-first order and the second-order kinetic models were applied to the data. The pseudo-first order rate expression popularly known as the Lagergren equation can be written as follows [36]:

$$\frac{dq_t}{d_t} = k_{ad}\,(q_e - q_t) \quad (7)$$

The linearised form of this equation after integrating and rearranging is:

$$\log\,(q_e - q_t) = \log q_e - k_{ad}\frac{t}{2.303} \quad (8)$$

where $q_e$ (mg/g) is the mass of metal ions adsorbed at time t and $k_{ad}$ is the first order rate equilibrium constant.

In order to obtain rate constants, the straight line plots of log ($q_e$ - $q_t$) against t (time) were made in Fig. 4. The plots gave fairly straight lines for the metal ion. The intercept of these plots should give log $q_e$. However, if the intercept does not equal to the equilibrium uptake of metal ions, the reaction is not likely to be first order even if the plots have high correlation coefficient with the experimental data [37]. The $R^2$ values, $q_e$ and $k_{ad}$ are presented on Table 2. The sorption data was also analysed in terms of a pseudo-second order mechanism [37] given by:

$$\frac{dq_t}{d_t} = k_2\,(q_e - q_t)^2 \quad (9)$$

Linearising and integrating gives:

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e} \quad (10)$$

where $h_o$ is the initial adsorption rate (mg/g min) = $k_2q_e^2$

If the second order kinetics is applicable, the plot of t/$q_t$ against t in the above equation should give a linear relationship from which the constants $q_e$ and $h_o$ can be determined. These were plotted in Fig. 5 for both biosorbents. The plots gave good fits to the experimental data considering the regression coefficients. This means that the sorption can be described better by a pseudo-second order rate equation, hence $q_e$ and $h_o$ were evaluated and presented in Table 2. The theoretical $q_e$ values for the two metal ions were also very close to the experimental values, all these suggest that the sorption followed the second-order kinetic model.

### 3.6 Effect of Initial Metal ion Concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration ($C_o$): at low concentrations, metals are adsorbed by specific sites while with increase in metal concentrations the specific sites are saturated and the exchange sites are filled [38]. The metal ion equilibrium level of African yam bean pod and groundnut shell is presented as a function of $Cr^{6+}$ in aqueous solution in Fig. 6.

From the graph, equilibrium uptake increased with increasing of initial metal ion concentration, $C_o$, at the range of experimental concentration. This is a result of the increase in the driving force of the concentration gradient [39], as an increase in the initial metal ion concentrations. In the same conditions, if the concentration of the metal

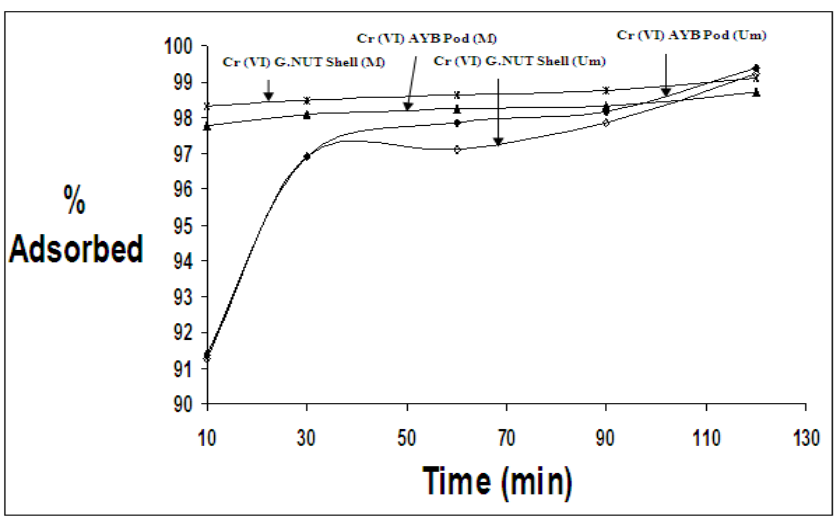


**Fig. 3. Variation of time on adsorption of Cr(VI) using modified and unmodified AYB Pod and G'NUT Shell**

ions in solution was bigger, the active sites of the biosorbents would have been surrounded by much more metal ions; so the values of $q_e$ increased with the increasing of initial metal ions concentration. The increase in sorption with concentration of $Cr^{6+}$ in aqueous solution may be attributed to increase in the amount of the adsorbate approaching the surface of the biosorbent. With the increase in biomass dose of both modified and unmodified African yam bean (AYB) pod and groundnut shell, the biosorption capacity per gram of biosorbents decreases. This is because the amount of metal ions was changeless in the system; the more the biomass use, the little the biosorption quantity adsorbed for per gram of biosorbents. However, sorption capacity was increased slightly with increase in biomass weight. However, the increase in the amount adsorbed with increase in biosorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the biosorbents. This trend therefore implies that at constant initial metal ion concentration, it is expected that the amount adsorbed may increase with biosorbent dose if the weight of adsorbent used is not enough to adsorb all the metal ions. As the biosorbent dose increases, it reaches a point when the weight of biosorbent used is in excess of the initial concentration, hence there will be no appreciable increase in the amount adsorbed. Similar results have been reported [40].

### 3.7 Adsorption Isotherm

The equilibrium of biosorption of chromium (VI) was modeled by using the Freundlich adsorption isotherm. The Freundlich isotherm was chosen to estimate the adsorption intensity of the adsorbents towards the adsorbate. It is represented by the equation:

$$q_e = K_F C_{eq} \frac{1}{n} \quad (11)$$

The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as [41]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_{eq} \quad (12)$$

Where $C_{eq}$ is the equilibrium concentration (mg/g), $q_e$ is the amount adsorbed (mg/g) and $K_F$ and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. Plot of ln $q_e$ against ln $C_{eq}$ gives straight lines from where $K_F$ and n are calculated.

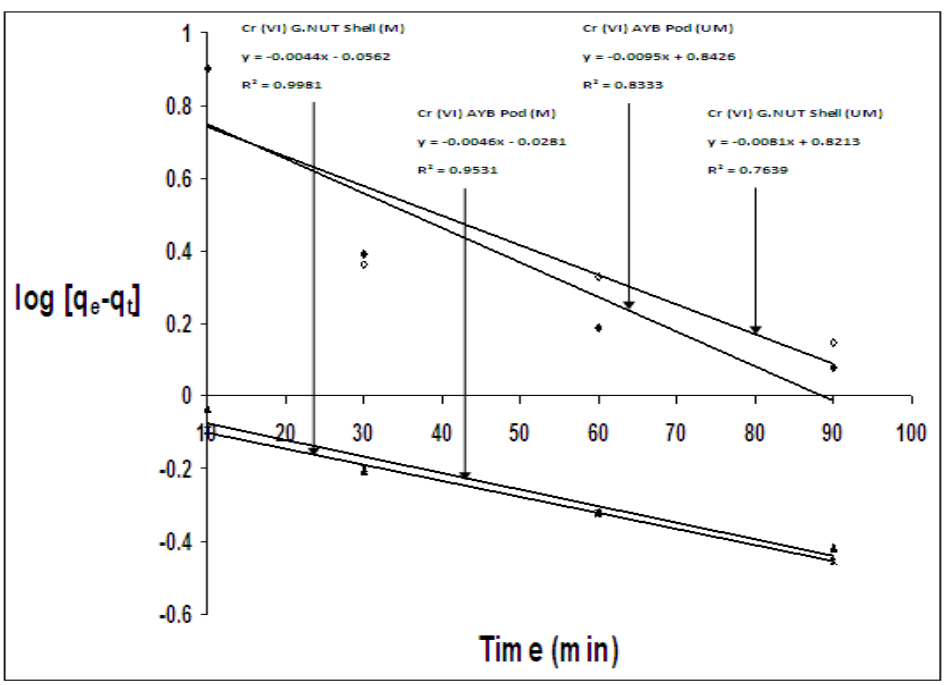


**Fig. 4. Pseudo-first-order plot for adsorption of Cr(VI) using modified and unmodified AYB Pod and G'NUT Shell**

**Table 2. Pseudo (Lagergreen) first and second order rate constants for $Cr^{6+}$ adsorption on modified and unmodified African yam bean pod and groundnut shell**

| Metal Ion | African yam bean pod | | | | | | Groundnut shell | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Modified | | | Unmodified | | | Modified | | | Unmodified | | |
| | First order | | | | | | | | | | | |
| | $K_{ad}(min^{-1})$ | $q_e$ (mg/g) | $R^2$ | $K_{ad}(min^{-1})$ | $q_e$ (mg/g) | $R^2$ | $K_{ad}(min^{-1})$ | $q_e$ (mg/g) | $R^2$ | $K_{ad}(min^{-1})$ | $q_e$ (mg/g) | $R^2$ |
| $Cr^{6+}$ | 0.011 | 0.94 | 0.9531 | 0.022 | 6.96 | 0.8333 | 0.010 | 0.88 | 0.9981 | 0.019 | 6.63 | 0.7639 |
| | Second order | | | | | | | | | | | |
| | $h_o$ (mg/g min) | $q_e$ (mg/g) | $K_2$ (g/mg min) | $h_o$ (mg/g min) | $q_e$ (mg/g) | $K_2$ (g/mg min) | $h_o$ (mg/g/ min) | $q_e$ (mg/g) | $K_2$ (g/mg min) | $h_o$ (mg/g min) | $q_e$ (mg/g) | $K_2$ (g/mg min) |
| $Cr^{6+}$ | 555.6 | 99.0 | $5.67x10^{-2}$ | -8.4 | 98.0 | $-8.7x10^{-4}$ | 555.6 | 99.0 | $5.67x10^{-2}$ | 89.3 | 100.1 | $8.9x10^{-3}$ |

**Table 3. Sorption isotherm constants and coefficients of determination of Cr(VI) ion for modified and unmodified African yam bean pod and groundnut shell**

| Metal Ion | Freundlich isotherm | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AYB Pod (Modified) | | | AYB Pod (Unmodified) | | | G'NUT Shell (Modified) | | | G'NUT Shell (Unmodified) | | |
| | $K_F$ | n | $R^2$ | $K_F$ | n | $R^2$ | $K_F$ | n | $R^2$ | $K_F$ | n | $R^2$ |
| $Cr^{6+}$ | 32.1 | 1.28 | 0.9956 | 20.85 | 1.11 | 0.6952 | 128.7 | 1.47 | 0.9268 | 35.61 | 1.44 | 0.8933 |

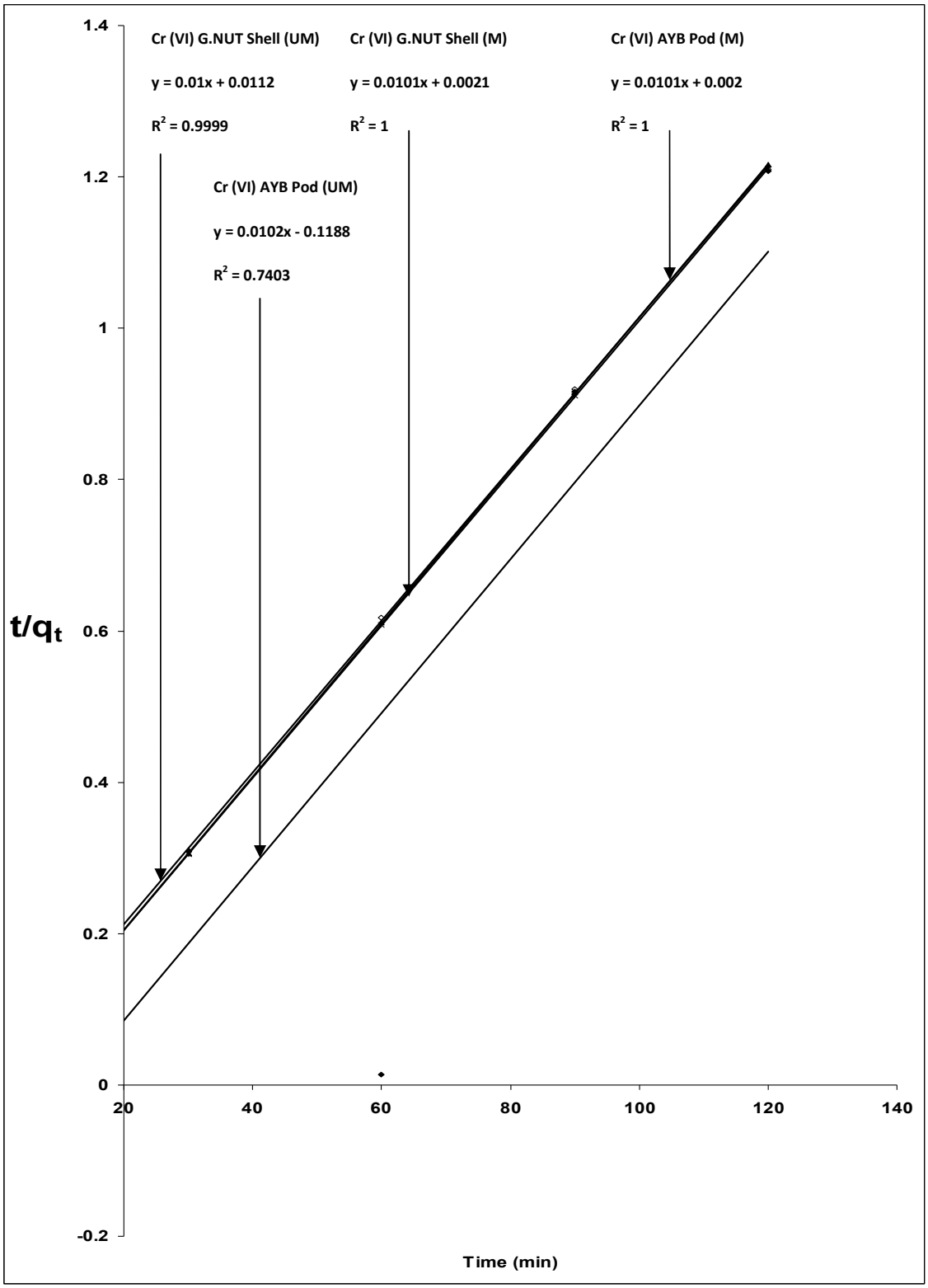


**Fig. 5. Pseudo-second-order plot for adsorption of Cr(VI) using modified and unmodified AYB Pod and G'NUT Shell**

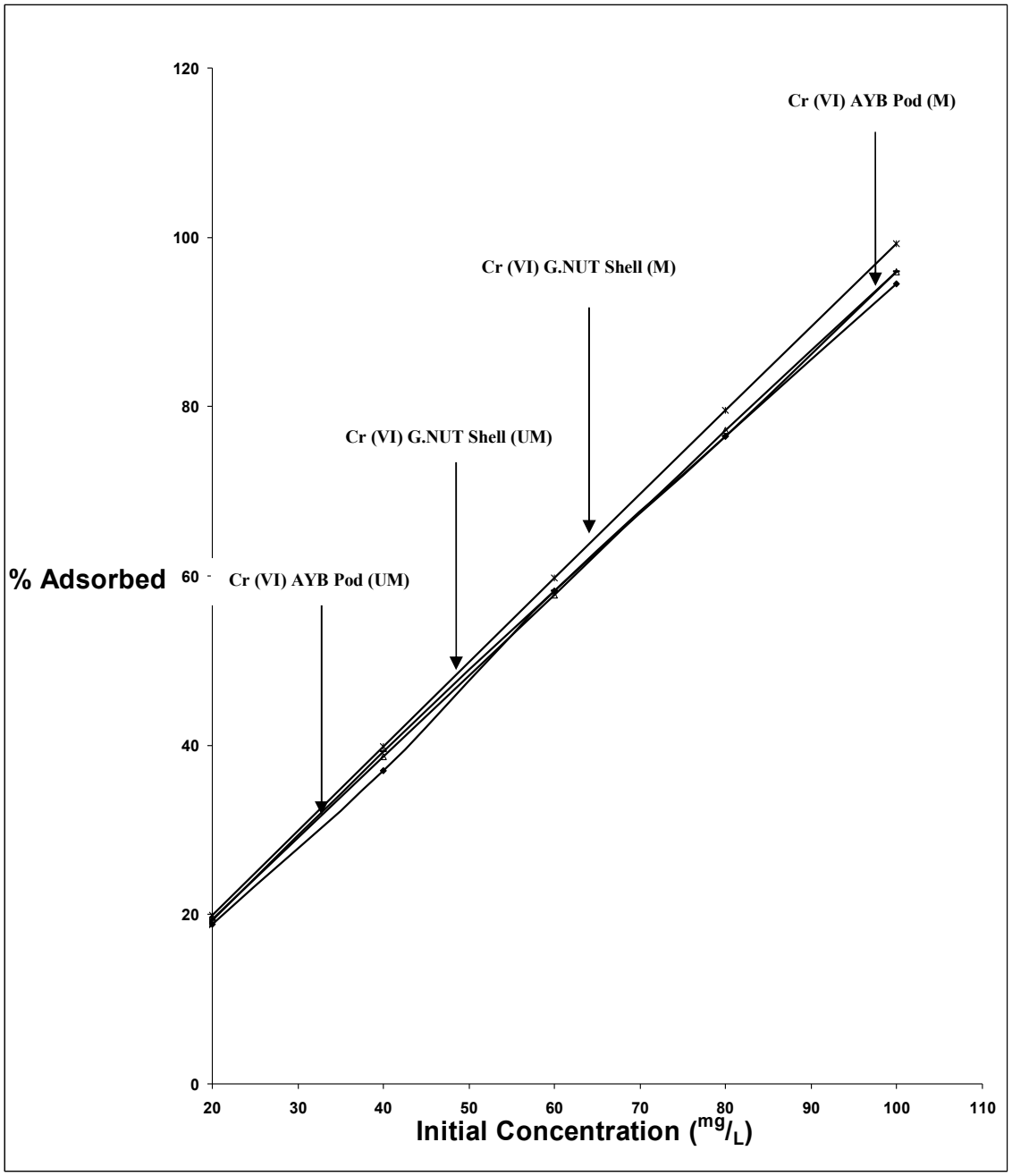


**Fig. 6. Varaition of initial concentration on adsorption of Cr(VI) using modified and unmodified AYB pod and G'NUT shell**

The values of $K_F$ and n were calculated from the intercepts and slopes of the Freundlich plots respectively and are shown on Table 3. According to Kadirvelu and Namasivayan [42], n values between 1 and 10 represent beneficial adsorption. Also, Akgerman and Zardkochi [43] stated that the values of $K_F$ and n determine the steepness and curvature of the isotherm. The value of 1/n less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa [44].

The magnitude of $K_F$ and n shows easy separation of heavy metal ions from wastewater and high adsorption capacity of metal ions onto the adsorbents. The value of n which is related to the distribution of bonded ions on the adsorbent surface is positive for the metal ions adsorption onto the two adsorbent types; this indicates favourable adsorption. Nonetheless, the higher the $K_F$ values, the greater the adsorption intensity. Therefore, the $K_F$ values which were higher for groundnut shell and also the modified adsorbents confirms that the adsorption capacity of groundnut shell and modified mediums were greater than that of AYB pod and unmodified medium.

## 4. CONCLUSION

From this study, oxalic acid modified and unmodified African yam bean pod and groundnut shell of 250 µm were used to adsorb $Cr^{6+}$ from aqueous solutions. The type of sorption taking place was investigated. The effect of temperature, pH, initial metal ion concentration and contact time were also investigated. It was observed that both biosorbents are capable of adsorbing $Cr^{6+}$ from aqueous solution.

From the experimental data, the following conclusions were made:

i) The uptake level of Cr(VI) ion by both adsorbents was above 90% by average and modification of the adsorbents enhanced slightly the adsorption process.
ii) The amount of metal ion adsorbed increased with increment in initial metal ion concentration.
iii) Increase in pH 2.0 to 6.0 increased the uptake level of the Cr(VI) ion but decreases at higher pH mainly for the modified adsorbents, while the uptake level became fairly constant for the unmodified adsorbents from pH 8.0 to 10.0.
iv) Increase in temperature from 303 K to 343 K reduced the uptake level of the ions suggesting an exothermic process.
v) The groundnut shell showed better adsorption capacity than the African yam bean pod; this may be attributed to the mesh-like structure of groundnut shell which creates more pores for metal ion biosorption.

All these showed that the use of African yam bean pod and groundnut shell in the removal of heavy metal ions is feasible. This will also help to reduce the amount of these wastes that liter our environment as well as help in keeping our environment clean.

## ACKNOWLEDGEMENT

The authors are most grateful to Engr. Dr. J.C. Igwe, H.O.D. Industrial Chemistry, Abia State University, Uturu, Nigeria for his invaluable assistance towards the completion of this research work.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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