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Extirpation of Chromium Ions from Aqueous Solution by Native Locust Beans

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Abstract: *This study focused on using native locust beans (Parkia biglobosa) hulls as an adsorbent of chromium ion from its aqueous solution by batch mode process, Atomic absorption spectrophotometer(AAS) was used in determining the metals concentration. Four factors affecting heavy metals sorption; pH,sorbent dosage, initial concentration and contact time were studied at 30±2 ℃ Optimum chromium ions extirpation was attained at pH 6 and 91.94% of chromium (VI) ions were removed in the first 60mins. Equilibrium sorption isotherms were evaluated, Freundlich model and Langmuir model results proved favourable sorption with the correlation coefficient (R^2)of 0.9784and 0.9492 respectively,but former isotherm equation better-definedadsorption process as compared to latter isothermequation. Lagergren pseudo-first-order and Ho pseudo-second-order kinetic models were employed, but chromium (VI) ions adsorption was better explained by Ho pseudo-second-order model.*

Keywords: *Parkia biglobosa,Chromium,Rich-lignocellulosic, Extirpation, Adsorption*

1. INTRODUCTION

A substantial amount of hazardous heavy metals found in our aquatic and terrestrial environment nowadays are the aftermath of indiscriminate discharges of heavy metals bearing effluents from industries, which is harmful to aquatic life and human health. Heavy metal has been known to be toxic environmental persistent contaminants, due to their nondegradableand mobility in natural water ecosystem [1]. Persistence of the arsenic, cadmium, chromium, cobalt, copper, lead, nickel, manganese, mercury and other heavy metals in the ecosystem and their incremental accumulation infood chain pose a negative impact on human health[3].Wastewater from electroplating, leather tanning, metallurgical, dyes,wood preservation, battery manufacturing industries contains chromium ions species. Trivalent and hexavalent are the prevalent chromium ions species found in chromium-related industrial waste streams, the toxicity of chromium to human health varies to its oxidation state and most toxic form of chromium is thought to be Cr^{+6}, because longtime exposure causes cell death, cell transformation and gene mutation[4],these are due to its mutagenic, teratogenic and carcinogenic properties [5,6]. United State Environmental Protection Agency has set 0.05mg/l as the maximum permissible limit of hexavalent chromium in drinking water[7].Based on high operational cost, ineffective at low metal concentration and a huge amount of metal-bearing sludge generates by conventional methods, such as Ion-exchange, reverse osmosis, solvent extraction, lime precipitation, activated carbon adsorption, electrolysis and membrane filtration methods in the extirpation of toxic heavy metals from industrial waste water. Consequently, a promising alternative absorption method by the use of inexpensive biological and low-cost available rich-lignocellulosic agro waste materials have been proved effective and efficient by many researchers for the sorption of trivalent and hexavalent chromium, lead, copper, zinc, mercury, cadmium and so forth, from the aqueous solution and industrial metal-bearing effluents, such as Africa star apple [8], Animal bones [9], *Azadirachta indica* bark [10], Bamboo root [11], Brown seaweed [12,13,14],Carrot residues [15], Crab carapace [16],Cocoa pod husk[17], Eggshell [18,19,20], Hazelnut shell[21], Maize bran [22], Non-living *Egeria densa* [23], Oak sawdust [24], Okra waste [25], Palm kernel fibre[26], Seed oil shell[27], Sugar beet pulp and fly ash [28], Sunflower stalks [29]. This study was conducted to evaluate the feasibility of Cr(VI) extirpation from aqueous solutions by rich-lignocellulosicnative locust beans hull agro-wastes.Four metal sorption influences parameters, kineticsand sorption isotherms were investigated.

2. MATERIALS AND METHODS

2.1. Sorbent Preparation

Native locust beans hull agro wastes were collected from locust beans food condiment production site in Agosasa, Ipokia local government Area, Ogun State, Nigeria. Locust beans hulls were extensively washed with deionized water. Then they were oven dried at 55^{O}C and grounded intoa powderyform, using pre-cleaned local mortar and pestle and sieved with a mesh to a maximum particle size of 2mm.

2.2. Preparation of Metal Ion Solution

Stock solution (1000mg/L) of chromium was prepared by dissolving the required amount of analytical grade $K_2Cr_2O_7$ in deionized and double distilled water. Working solution (100mg/dm^3- 500mg/dm^3) concentrations of Cr(VI) ions were prepared by serial dilution of the stock standard solution with double distilled water.

2.3. Batch Experiments

The batch experiments were conducted in 100 mL Erlenmeyer flasks containing 25 mL of chromium solution. A weighed amount of native locust beans hull was added to chromium solutions. The mixtures were shaken on a rotary shaker at 130 rpm for 1 h at 30±2°C. The effect of pH (4.0-9.0), initial metal concentration (100-500 mg/L),sorbent dosage (0.4-2.4 g/L) and contact time (30-180 min) was investigated in order to find the optimum conditions for the chromium metal biosorption.

After equilibrium, the solution suspensions were filtered and the supernatants were subsequently analyzed for residual Chromium concentration with atomic absorption spectrophotometer (AAS; Perkin-Elmer model Analyst 2000).

Amount of metal adsorbed by1.0g of the biomass was calculated from the following mass balance equation:

$$q = \frac{C_o - C_e}{1000} \frac{V}{W} \tag{1}$$

Where:

q is the amount of metal uptake (mg/g)

C_o and C_e are the initial and final metal ion concentration (mg/L

M is the amount of native locust beans hull (g)

V is the volume of the solution (mL).

The Chromium concentration removal percentage can be calculated as follows:

$$\% \text{ removal} = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \tag{2}$$

Where C_t (mg/l) is liquid-phase concentration of Cr (VI) ion at time t.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

pH of the metalsolution is an important parameter that affects metal adsorption/loading by influencing the surface properties of biomass, metal speciation in solution and degree of ionization [30].The effect of pH on the percentageof chromium metalextirpated from aqueous solution by native locust bean hull is illustrated in Fig.1.Increase sorption percent observed from pH 4 to pH 6 and decrease significant soption changes occurs when metal solution becomes neutral as pH is 7 to basic medium ofpH 8 and pH 9 respectively, while chromium metal precipitate observed, that can be due to increasing OH^- ions in the adsorption medium, as earlier reported in our previous research paper [31]. Therefore, Optimum sorption of 97.3% attained at pH 6, with these observations, further experiments were performed at pH 6.

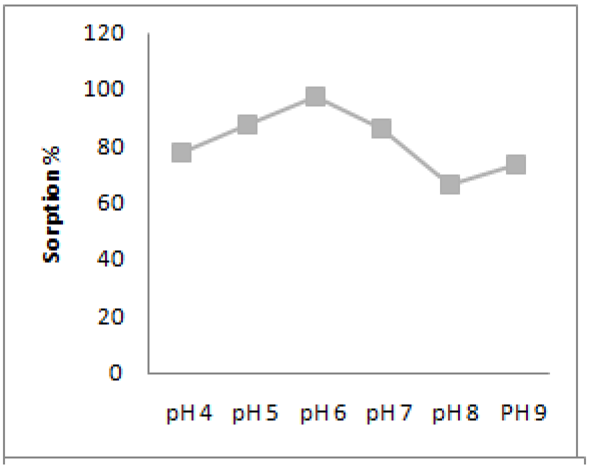

Fig1. *Effect of pH on Cr^{6+} sorption by nativebeans hull, pH 6 at 30±2℃*

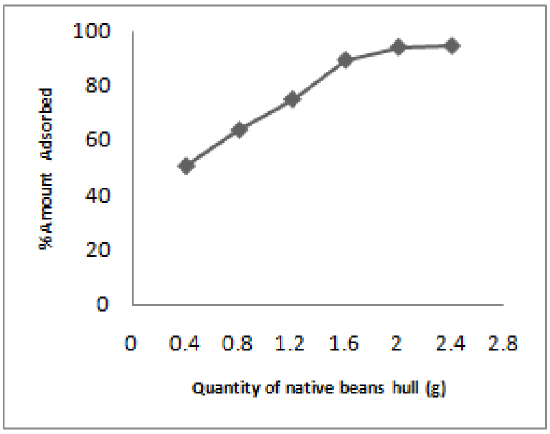

Fig2. *Effect of dosageon Cr^{6+} sorption by nativelocust locust beans hull, pH 6 at 30±2℃*

3.2. Effect of Sorbent Dosage

Fig. 2 shows the plot of the amount of chromium adsorbed(q_e)versus quantity of native beans hull (g)examined. From theplot,it can be observed that increase amount of metal ions uptake was achieved with the increase in adsorbent quantity. It implies that at high sorbent dosage, the available metal ions are sufficient to cover all the exchangeable sites on the native bean shull usually resulting in high metal ion uptake. Such a trend is mostly attributed to an increase in thesorptive surface area and the availability of more active binding sites on the surface of the adsorbent [32].

3.3. Effect of Initial Metal Concentration

The feasibility and efficiency of a biosorption process depend not only on the properties of the biosorbent, but also the concentration of the metal ion solution. The adsorption percentage of chromium metal extirpated per gram of native locust beans hull from initial chromium metal chemistry in solution and decreases in metal sorption capacity as initial metal ion concentration increases from 100mg/L to 500mg/Lin order of 97.3% <92.7% < 89.5% < 80.8% <80.5%.Thus, the higher initial metal ion concentration the lower metal sorption per gram of native locust beans hull.

However, the optimal soption value obtained from lower chromium chemistry in solution indicates that all metal ions present in solution interacted more with the binding sites than at higher metal ions concentrations and low sorption at higher metal chemistry in solution suggests agglomeration of adsorbent particles[33]. This agglomeration elongates diffusion path length and decreases the total available surface area of native locust bean hull particles for sorption.

3.4. Effect of Contact Time

The native locust beans hull exhibited optimum adsorption capacity within the first 60min of contact time, no significant sorption changes observed throughout the selected contact time. This assumed that all available active binding sites of native locust beans hull have been saturated before the180mins of the investigation. Therefore, the contact time of 60min was selected as the optimal contact time for further experiments.

3.5. Sorption Kinetic Model

Lagergren model [34]and Ho and McKay models [35] were used to determine the sorption kinetic of the study.

Lagergren model equation can be expressed as:

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1 t}{2.303} \tag{3}$$

Where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min), q_e is the amount of metal ions adsorbed (mg/g) at equilibrium and k_1 is the pseudo-first-order reaction rate constant for adsorption (min^{-1}).

The Ho pseudo-second-order equation as:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \tag{4}$$

Where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min), q_e is the amount of metal ion adsorbed (mg/g) at equilibrium and k_2 is the Ho pseudo-second-order reaction rate constant for adsorption(g $(\mathrm{mgmin})^{-1}$).

$$h = k_2 {q_e}^2 \tag{5}$$

In equation (5), h can be regarded as the initial sorption rate as q/t when t approaches zero.

3.6. Isotherm Model

Langmuir and Freundlich's models were used to analyze isotherms adsorption data and equation (6), (7), (8) and (9) below give details respectively.

$$q = \frac{KC_e b}{(1 + KC_e)} \tag{6}$$

Where, C_e is the equilibrium solution phase concentration (mmol kg^{-1}), q the equilibrium solid phase concentration (mmol kg^{-1}), k is the enthalpy related constant, b is the Langmuir isotherm sorption capacity (mmol kg^{-1}).

Linearized form of equation 6 written as:

$$\frac{C_e}{q} = \frac{1}{K_b} + \frac{C_e}{b} \tag{7}$$

Fig. 5show the plot $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ that gives Langmuir isotherm, where $\frac{1}{b}$ is the slope and $\frac{1}{K_b}$ is the intercept.

Equations (8) and (9) give non-linear and linear Freundlich equations respectively.

$$q_e = K_f {C_e}^{1/n} \tag{8}$$

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{9}$$

Where K_f is the sorption capacity constant and n is the intensity constant, qe and Ce are the same as earlier stated in equation 6.

1/n, n, K_f and R^2 results presented in the Table. 1were calculated from the Plot of Logq_e versus Log C_e shown in Fig. 6, where the slope is the value of 1/n and intercept is equal to Log K_f.

Table1. *Langmuir and Freundlich isotherms parameters for the adsorption of metals by nativethe locust beans hull*

Metal	Langmuir isotherm parameters				Freundlich isotherm parameters		
B	Qmax	K_L	R^2	1/n	n	K_f	R^2
Cr	8.46	0.064	0.9492	0.42	2.384	1.57	0.9784

Table2. *Pseudo-first and second order parameters for the adsorption of the metal ion by the native locust beans hull*

Metal	Pseudo-first order parameters				Pseudo-second order parameters				
	q_e(cal)mg/g	K_1 (1/min)	R^2	q_e(exp)mg/g	q_e(cal)mg/g	h(mg/g.min)	K2(g/mg.min)	R^2	qe(exp)mg/g
Cr	0.0228	-0.0187	0.2127	2.3010	2.1872	0.27	0.056	0.8761	2.3010

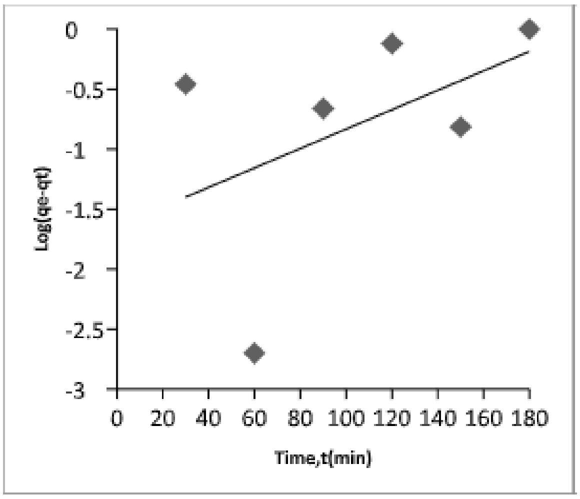

Fig3. *Pseudo-first-order for the adsorption of Cr^{6+}onto locust beans hull.native locust beans hull*

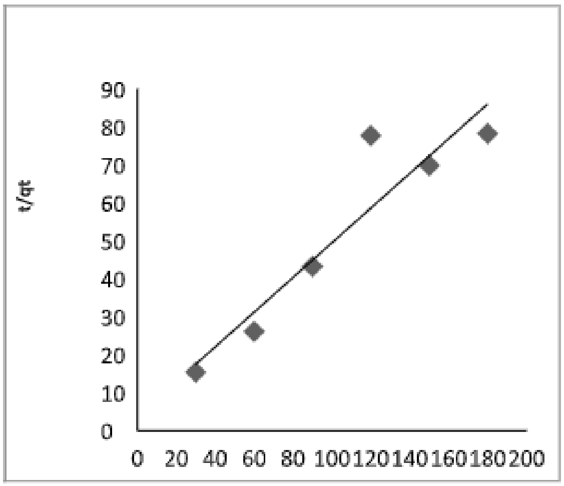

Fig4. *Pseudo-second-order for the adsorption of Cr^{6+}onto native locust beans hull.native locust beans hull.*

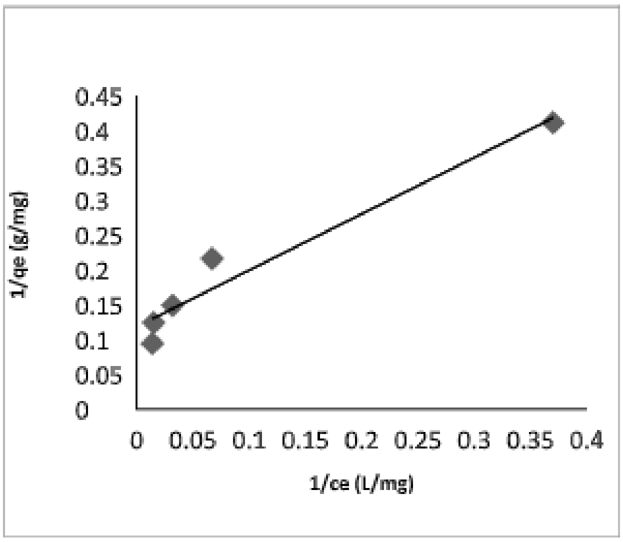

Fig5. *Langmuirsorption isotherms of Cr^{6+}ontothe locust beans hullbeans hull*

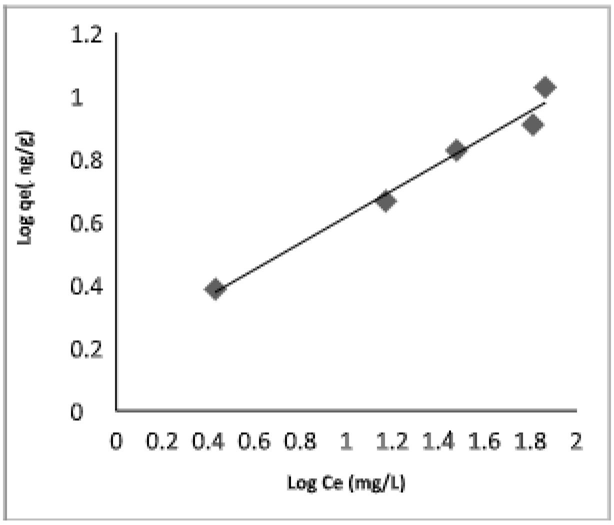

Fig6. *Freundlichsorptionisotherm of* Cr^{6+}*ontothe locust beans hullbeans hull*

The experimental data analyzed by Langmuir and Freundlichisotherm models are shown in table 1, and the isotherm data fitted well to the Freundlich isotherm with heterolayer adsorption capacity of 1.57mg/g. This evidence agrees with the Freundlich adsorption prediction that the solute concentrations on the adsorbent will increase so long as there is an increase in the solute concentration in the aqueous solution. The adsorption isotherms exhibited the Freundlich behaviour, which indicates a heterogeneous surface bonding [36]. The results suggest that the sorption of chromium metal can be characterized by heterolayer formation of the metal ions on the surface of the sorbents

Similarly, as seen in table 2, the correlation coefficient and other parameters values of pseudo-first-order kinetic are lower than in the case of the pseudo-second-order kinetic model. Thus, experimental data were fitted by the second-order kinetic model, which indicated that chemical sorption was the rate-limiting step,inside of mass transfer.

Zhang et al.[37] revealedthatn value between 1 and 10 represent beneficial adsorption, thus, n value in this research proved adsorption tendency of native locust beans hull and a large value for 1/n indicates a larger change in effectiveness over different equilibrium concentration and the relative energy distribution on the adsorbent surface.

Consequently, the values 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 [38]. In this research work, the value of 1/n obtained found to be less than unity, which agrees with the results discussed above that 1/n value indicates that the relative distribution of energy sites depends on the nature and strength of the adsorption process.

4. CONCLUSION

The feasibility, efficiencyand potential usefulness of native locust beans hull as an inexpensive solid adsorbent for chromium ion(Cr^{6+})have been proved in this work.Freundlich model and Langmuir model results proved favourable sorption with the correlation coefficient (R^2)of 0.9784 and 0.9492 respectively, but former isotherm equation better defined the adsorption process as compared to latter isotherm equation,which indicates a heterogeneous surface bonding. The maximum biosorption capacity oflocust beans hull has been found to be 8.46mg Cr(VI)/g of the dry weight ofbiomass. Future studies will be conducted to evaluate the effectiveness of natural and modified locust beans hullas a sorbent on heavy metal extirpation and recovery from contaminated wastewater.

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