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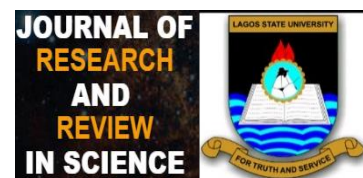
The Kinetics and Thermodynamics studies of the biosorption of Chromium (III) ions from aqueous solution using groundnut husk

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Abstract:
Introduction: The biosorption of Cr (III) ions from aqueous solutions by groundnut husk, a low-cost biosorbent was studied on a laboratory scale batch experiments. The effects of pH, contact time, particle size, biosorbent dosage and temperature on the adsorption of Cr (III) ions were investigated.
Materials and Methods: Determination of Chromium ion concentration in solution was done using Atomic Absorption Spectrophotometer (AAS).
Results: The results show that the removal mechanism is predominantly by chemisorption and it is dependent on the physical and chemical characteristics of the biosorbent material. From the initial concentration of 0.5 mM, optimum Cr (III) ions removal was obtained at pH of 4, particle size of 0.15 nm, contact time of 180 minutes and biosorbent dosage of 50 mg, with the highest biosorption efficiency of 81.15 %. The biosorption process was best described by the BET adsorption isotherm with R2 value 0.9814 indicating multiplayer adsorption.
Conclusion: Analysis of the experimental data revealed that the biosorption of Cr (III) ions from aqueous solution by groundnut husk is a spontaneous process with a ΔG^o value of -24.38 kJmol-1 at 298 K and follow the pseudo second order kinetics with a rate constant of 0.0151 min-1. The results indicate that groundnut husk can be employed as a low cost alternative to commercial adsorbents in the removal of Cr (III) ions from wastewater
Keywords: Biosorption, Groundnut husk, BET Isotherm, Spontaenous process

All co-authors agreed to have their names listed as authors.

1. INTRODUCTION

(Pollutants interact naturally with biological systems. The most problematic pollutants include heavy metals, pesticides and other organic compounds which can be toxic to wildlife and humans in small concentration [Ahalya, N. et al., 2003]. In recent years, extensive attention has been paid on management of environmental pollution caused by hazardous materials such as heavy metals, synthetic dyes and non-biodegradable polymer materials. Heavy metal pollution has become one of the most serious problems, and the presence of these metals even in trace amounts is usually toxic and detrimental to both flora and fauna [Wang, J. 2002]. Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics.

A number of methods have been developed for the removal of heavy metals from liquid wastes such as precipitation, evaporation, ion exchange, membrane processes, etc. However, these methods have several disadvantages such as unpredictable metal ion removal, high reagent requirement, generation of toxic sludge, etc. Therefore, the need for economical and effective methods for removing heavy metal from wastewater has resulted in search for other materials that may be useful in reducing the level of heavy metals in the environment. Biosorption, an environmental friendly way of metal removal has been employed for sometimes now. It involves the accumulation and concentration of heavy metals from aqueous solution using biological materials based on the metal binding capacities of the biological materials. [Stirk, W. A. et al., 2000]. Heavy metals removals have been achieved by adsorption on different materials such as activated carbon, agricultural waste, minerals, bacteria e.t.c. It is advisable that the adsorbent is available in large quantities, abundant in nature, easily regenerable and economical. The toxicity and bioaccumulation tendency of heavy metals in the environment is a serious threat to the health of living organisms. Unlike organic contaminants, heavy metals cannot be broken down by chemical or biological processes; they can only be transformed into less toxic species. Due to the noxious effects of these metals, there are growing environmental and public health concerns, and a consequent need for increase awareness in order to remediate the heavy metal polluted environment. [Ayansina S. A. et al., 2017]. Among the heavy metals, chromium is of great environmental concern because of its application in many industrial sectors such as electroplating, metal corrosion resistance, leather tanning, metal finishing, chromate preparation, cement, dyeing, wood preservatives, paint and pigments, textile dyeing and steel fabrication [Hadjmohammadi et al. 2011]. For example, in the chromium tanning process, the leather takes up only 60–80 % of the applied chromium, and the rest is usually discharged into the sewage system causing serious environmental hazard. Chromium ions in liquid tanning waste occur mainly in trivalent form, which gets further oxidized to hexavalent chromium form, due to the presence of organics [Sarin and Pant 2006].

Biosorption is a physico-chemical and metabolically-independent process based on a variety of mechanisms including absorption, adsorption, ion exchange, surface complexation and precipitation. Biosorption processes are highly important in the environment and conventional biotreatment processes. Biosorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals and dyes from large amount of industrial wastewaters [Oboh, I. et al., 2009]. The understanding of the mechanisms of metal biosorption now allows the process to be scaled up and used in field applications, with packed-bed sorption columns being perhaps the most efficient for this purpose. Regenerating the biosorbents increases the process economy by allowing their reuse in multiple sorption cycles. The process results in metal-free effluents and small volumes of solutions containing concentrated metals, which can be easily recovered. [kratochvil D. 1998].

In view of the economic and environmental advantages of biosorption over the conventional methods, the technique is now being optimized on industrial scales for the removal of toxic pollutants such as heavy metals, organic and synthetic dyes from industrial effluents. This present study therefore investigates the mechanisms and conditions for optimum removal Cr (III) ions from aqueous solution using the groundnut husk as the biosorbent.

2. MATERIAL AND METHODS

Groundnut husk was collected from a local market in Ilorin, washed and rinsed with distilled water and laid flat on clean table to dry. After drying it was grounded in smaller particle which was then sieved using a mesh of size 0.15 mm and stored in plastic bag.

2.1 CHARACTERIZATION OF THE BIOSORBENT

The biosorbent was characterized using FTIR and Scanning Electron Microscope (SEM). The metal residual in the solution was determined by Atomic Absorption Spectroscopy (AAS). The metal uptake capacity (amount of removal of chromium ion) and the adsorption capacity (percentage of chromium ion removal) were calculated using the following equations:

Metal Uptake Capacity = *Initial Chromium ion conc. – Final Chromium ion conc.* . …. (1)

% Chromium (III) adsorbed =

$$\frac{\textit{Metal uptake capacity}}{\textit{initial chromium ion conc.}} \times 100 \quad .... (2)$$

2.2 Preparation of Aqueous Salt Solution

An aqueous stock solution (0.5 mM) of Chromium (III) ion was prepared using analytical grade Chromium(III) nitrate salt ($Cr(NO_3)_3.9H_2O$) as follows; 0.4001 g of $Cr(NO_3)_3.9H_2O$ was dissolved and made to mark with distilled water in a 2 litre standard volumetric flask and was kept in an amber bottle to prevent photolysis.

2.3 Batch mode Adsorption Experiment

Batch mode adsorption studies were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing biosorbate and biosorbent was taken in a bottle and agitated at 200 rpm in a mechanical shaker at predetermined time intervals, after which they are centrifuged at 8000 rpm for 10 minutes to separate the supernatant.

For each experiment, 25 ml of 0.5 mM aqueous solution of Cr (III) ions (concentration was varied in the case of effect of initial concentration) was agitated with 50 mg of Pulverized groundnut husk (except for effect of biosorbent dose, where the mass was varied) at a constant speed of 200 rpm for 3 hours in a shaker after which they were centrifuged at 4,000 rpm for 20 minutes to separate the supernatant. The experiments were carried out in triplicate after which 5 ml of each supernatant is taken and analyzed for the residual metal ions content by AAS

The effect of initial metal ion concentrations on the biosorption process was determined in the range 0.1 – 5.0 mM Cr (III) ions concentration. The effects of the initial pH on the biosorption capacity were investigated in the pH range of 2 – 9. The effect of time on biosorption process was studied at the time range of 2 – 7 hours contact time. The effect of biosorbent dose on the biosorption process was studied using 10 - 110 mg of the biosorbent. The effect of temperature on the biosorption process was studied at a temperature range of 25 – 60 ºC

3. RESULTS AND DISCUSSION

3.1 Characterization of the Biosorbent

The surface area of the biosorbent as well as its chemical composition and the functional groups present on it play vital roles in the biosorption process. These were characterized using Scanning Electron Microscope (SEM) analysis, Energy-dispersive X-ray (EDX) analysis and Fourier Transform Infrared Spectroscopy (FTIR).

3.1.1 Scanning Electron Microscope (SEM) Analysis

SEM of the groundnut husk was obtained using a Nova NanoSEM scanning electron microscope to study the morphological microstructures of the biomaterial in terms of surface roughness and porosity. The micrographs for the biosorbent before and after the biosorption process were taken at different magnification of 100 μm, 20 μm and 2 μm as shown in Fig. 1.
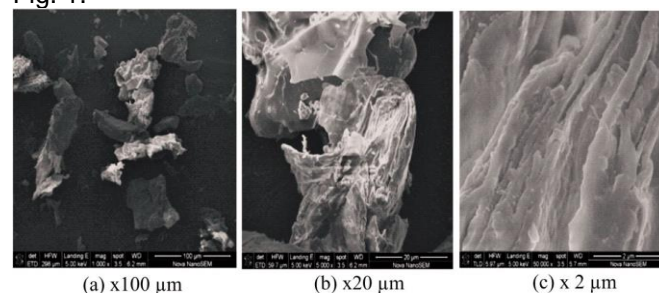

(a) x100 μm   (b) x20 μm   (c) x 2 μm

Fig. 1. The SEM of the groundnut husk

3.1.2 Energy-dispersive X-ray (EDX) Analysis

Energy-dispersive X-ray (EDX) was used for the elemental analysis and chemical characterization of the groundnut husk. The result shows a mean value of 63.7% carbon, 35.4% oxygen, 0.5% potassium and 0.4% calcium. Fig. 2 shows the spectra which indicate the peaks corresponding to the elements making up the true composition of the groundnut husk.
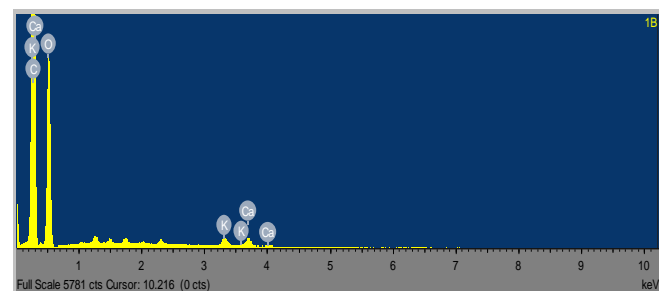

Fig. 2. Energy-dispersive X-ray (EDX) spectra of the groundnut husk

3.1.3 Fourier Transform Infrared Spectroscopy (FTIR) studies

The Crude and spent samples of groundnut husk were subjected to Fourier Transform Infrared Spectroscopy analysis. The spectra obtained for the biosorbent before and after the experiments are presented in Figs. 3(a) and 3(b) respectively.
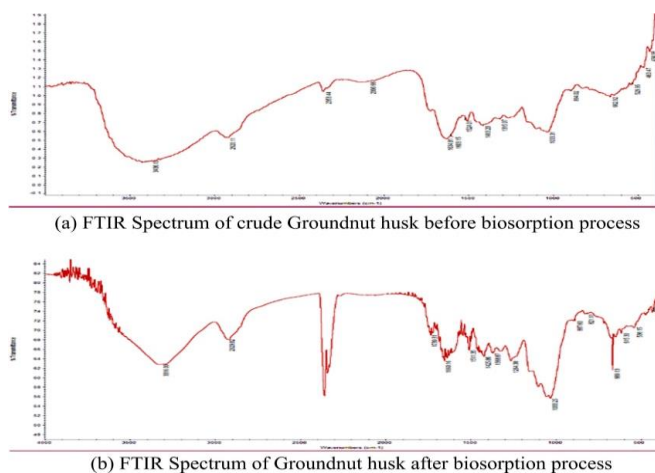
(a) FTIR Spectrum of crude Groundnut husk before biosorption process

(b) FTIR Spectrum of Groundnut husk after biosorption process

Fig. 3. FTIR of the groundnut husk

3.2 Batch Mode Adsorption Experiment

3.2.1 Effect of pH
pH is an important parameter in biosorption process, since it is responsible for protonation of metal binding sites. The experiments were carried out at different pH values 2, 3, 4, 5, 6, 7, 8 and 9 other parameters being kept constant. The results are as presented in Fig. 4(a).

3.2.2 Effect of initial metal concentration
The initial metal ion concentration is one of the factors that affect the efficiency of the biosorption process. The experiments were done with variable initial Cr (III) ions concentration (0.1, 0.2, 0.3, 0.5, 0.75, 1.0 mM) and constant temperature 25ºC, pH 4, contact time of 3 hours and 50 mg of 0.15 mm adsorbent. The experimental results of the effect of initial chromium concentration on removal efficiency are presented in Fig. 4(b).

3.2.3 Effect of contact time
Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Therefore, it is important to study its effect on the capacity of retention of Cr (III) ions by groundnut husk adsorbent. The effect of contact time on Cr (III) ions adsorption efficiency is shown in Fig. 4(c).

3.2.4 Effect of adsorbent dose
To study the optimum adsorbent dose, the experiments were conducted under the conditions of pH 4.0 and variable ad¬sorbent dose (10, 30, 50, 70, 90, 110 mg) in 25 ml of 0.5 mM standard solution, temperature 25 ºC and contact time 3 hours as shown in Fig. 4(d).
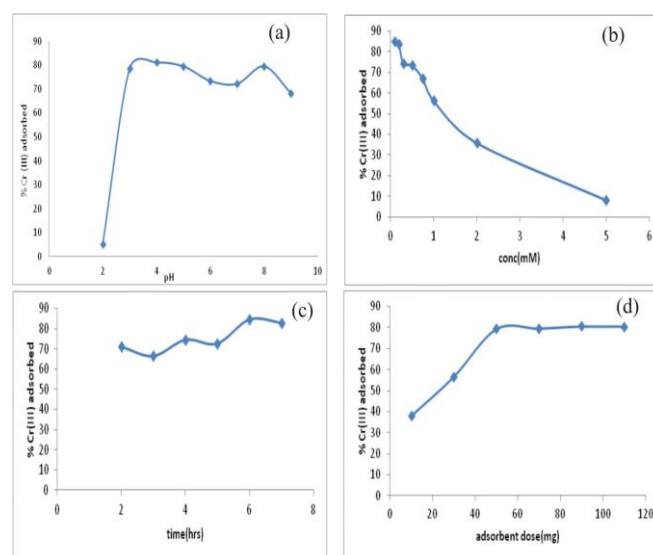

Fig. 4. Effects of (a). pH, (b). Initial Metal ion Concentration, (c). Contact time and (d). Biosorbent dose on biosorption of Cr (III) ions

3.2.5 Effect of temperature
Temperature is one of the effective factors on adsorption efficiency. The experiments were done variable temperature of 25, 30, 35, 40, 45, 50, 55 and 60 ºC other factors being kept constant at pH 4. The result as shown in Fig. 5(a) shows that the maximum adsorptions of Cr (III) ions by the groundnut husk were obtained at higher temperatures (40 – 60 ºC).

3.3 Adsorption Isotherm
Adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir [Langmuir, 1918], Freundlich [Freundlich, 1906], Temkin [Temkin and Pyzhev, 1940] and BET [Brunauer et al., 1938] models were used to describe the equilibrium data. The adsorption of Cr (III) ions onto groundnut husk can best be described by BET isotherm based on the correlation coefficient values obtained. The order of fitness is BET > Temkin > Freundrich > Langmuir. Adsorption isotherm is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents.

Table 1. Adsorption isotherm constants and parameters for Cr (III) ions adsorption onto the groundnut husk

Langmuir coefficients		Freundlich coefficients		Temkin coefficients		BET coefficients	
q_m (mg/g)	-147.1	K_f (mg/g)	1.2	B(kJ/mol)	14.0	K_B (kJ/mol)	-4.2
K_L (L/mg)	-8.09×10^{-3}	1/n (L/mg)	1.06	K_T (K/mg)	0.303	q_m (mg/g)	0.0145
R^2	0.031	R^2	0.8195	R^2	0.8388	R^2	0.8814

3.4 Kinetic Studies

The kinetics of an adsorption is probably the most important factor in predicting the rate at which adsorption takes place for a given system. Kinetics of adsorption is the tool used to examine the mechanism of adsorption process such as chemical reaction and mass transfer, a suitable model is needed to analyze the rate data. The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently used in the literature to predict the mechanism involved in the sorption process [Ho and McKay, 1998]. They were both used to test the adsorption kinetic model of Cr (III) ions onto groundnut husk. Both models were examined for suitability using their correlation coefficient, R2. Comparison of the two model revealed that the adsorption of the Cr (III) ions could be best explained using the pseudo-second order. This was due to the higher correlation regression coefficient R2 value.

3.4.1 Pseudo first order model

The Lagergren's first order model is expressed by the equation

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad \ldots\ldots\ldots (3)$$

Where q_t and q_e (mg/g) are respectively the amounts of sorbed metal at time t and at equilibrium respectively and k_1 (min^{-1}) is the first order rate constant. The linear form of the equation

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

Adsorption rate constants (k_1) and adsorption capacity (q_e) for the adsorption of Cr (III) ions by groundnut hust were calculated from the slope and intercept of the plots of $log(q_e - q_t)$ against t.

3.4.2 Pseudo second order model

This model is expressed by the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \ldots\ldots\ldots (5)$$

Where k_2 is the rate constant of pseudo-second-order model (g/mg min). Definite integration of the above equation for boundary conditions $q_t = 0$ when $t = 0$ and $q_t = q_t$ at $t = t$, give the following form of equation:

$$\frac{t}{q_t} = \frac{1}{(K_2 qe^2)} + \frac{1}{q_t}t \quad \ldots\ldots\ldots (6)$$

The equilibrium adsorption capacity (q_e) and the pseudo-second order rate constants k_2 were obtained from the slope and intercept of the plots of t/q_t against t for the biosorbents.

Table 2. Adsorption kinetics constants for Cr (III) ions adsorption onto groundnut husk

Pseudo first order coefficients		Pseudo second order coefficients	
K_1 (min^{-1})	1.15×10^{-3}	K_2 (g/mg min)	1.51×10^{-2}
q_e (mg/g)	3.43	q_e (mg/g)	3.43
R^2	0.712	R^2	0.9713

3.5 Thermodynamics Studies

The thermodynamics parameters such as standard Gibbs free energy change (ΔG^o), standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) were also studied in order to study the feasibility of the adsorption process and the effect of temperature on the adsorption of Cr (III) ions. This will be evaluated from the following equations:

$$K_c = \frac{c_{Ae}}{c_e} \quad \ldots\ldots\ldots (7)$$

$$\Delta G^0 = -RT \ln K_c \quad \ldots\ldots\ldots (8)$$

$$log K_C = \frac{\Delta S^0}{2.303 R} - \frac{\Delta H^0}{2.303 RT} \quad \ldots\ldots\ldots (9)$$

Where, K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium (mg/L). ΔG^o, ΔH^o, and ΔS^o are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (kJ/mol/K), respectively. R is the gas constant (8.314 J/mol/K) and T is the temperature (K).

The values of ΔH^o and ΔS^o (Table 3) were determined from the slope and the intercept of Van't Hoff plots of log K_c versus 1/T [Mohan and Singh 2002]. The thermodynamic plot is shown in Fig. 5(b).
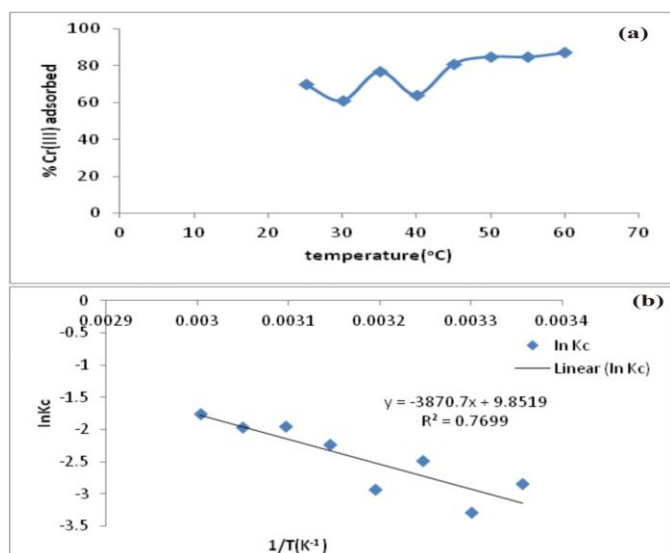
Fig. 5. (a). Effects of temperature on biosorption of Cr (III) ions and (b). Thermodynamic plot of Cr (III) ions onto groundnut husk

Table 5.   Thermodynamic parameters for the adsorption of Cr (III) ions onto groundnut husk

ΔH°	ΔS° (kJmol^{-1}K^{-1})	ΔG° (kJmol^{-1})							
		298K	303K	308K	313K	318K	323K	328K	333K
+32.2	+81.9	-24.4	-24.8	-25.2	-25.6	-26.0	-26.4	-26.8	-27.2

4. CONCLUSION

4.1 SEM Analysis
The micrographs clearly show the ruffled surface of the biomaterials. This indicates a porous medium, which is advantageous to the adsorption process, as there is a greater surface area available for adsorption.

4.2 FT-IR Analysis
The spectrum of the biosorbent before adsorption Fig. 3(a) reveals the presence of several functional groups on the surface of the biosorbent. The broad band in the region around 3436 cm^{-1} is assigned to the surface hydroxyl groups of bonded carboxylic acid and N-H bond. The O–H stretching vibrations occurred within a broad range of frequencies indicating the presence of free hydroxyl groups and bonded O–H bands of carboxylic acid (Han *et al.,* 2006).The asymmetric C–H stretching of surface methyl groups usually present on the lignin structure is observed at 2920 cm^{-1}. The

characteristic peaks due to the C–O group of carboxylic and alcoholic groups were present at 1033 cm^{-1} [Krishnani *et al.,* 2008]. The –O–H, -N–H, carbonyl and carboxylic groups have been reported as very important sorption sites for metal ions [Kalaivani *et al.,* 2014]. The other peaks at 1524 cm^{-1}, 1315cm^{-1}, 1413 cm^{-1} and 1634cm^{-1} can be associated with aromatic ring stretching, C-N amine group, C-H bond and C=O (amide) group respectively. The band at 2090 cm^{-1} indicates the presence of alkyne group which a very reactive group and can react with the metal. But there are some additional peaks in the FT-IR spectrum of the spent biosorbent after the experiment.

The new peaks at 1739 cm^{-1} and1264 cm^{-1} are due to the presence of a C=O bond of an aldehyde group and C–O bond of an ester group. This indicates the involvement of ester carbonyl and aldehyde carbonyl groups in the adsorption of Chromium (III).

4.3 Effect of pH
From the result, Fig. 4(a), it was observed that the optimum Chromium removal efficiency of 81.2% was achieved at the pH of 4. The percentage removal of Cr (III) ions increases from the pH of 2 to 4 and suddenly decreases as the pH increases. The lower percentage removal of Cr (III) ions observed at pH 2 could be attributed to the competition between protons and Cr (III) ions for the available binding sites of the biosorbent. It is expected that at a low pH, the biosorbent sites are majorly occupied by protons and the Cr (III) ions cannot easily become bound to these sites [Bradl, H. B., 2004]. However, at high pH, decrease in percentage removal of Cr (III) ions was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately lead to the reduction in sorption capacity [Baral *et al.,* 2006]. Furthermore, the adsorption of Cr (III) ions is qualitatively shown to be a cationic-exchange (chemisorption) process between Cr (III) ions and protons of the adsorbent carboxyl groups (Cr^{3+} and CrOH^{2+}), as indicated by [Bradl, H. B.,2004]. The results are similar to that reported by [William J. S. *et al* 2016].

4.4 Effect of pH
It is evident from Fig. 4(b) that, Cr (III) ions removal efficiency decreases with the increase in initial Cr (III) ions concentration. In case of lower Cr (III) ions concentrations, the ratio of the initial number of moles of Cr (III) ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, when the Cr (III) ions concentration is sufficiently large, the adsorbent's surface got occupied and the efficiency starts to decrease and the molecules desorbed from the adsorbent's surface. At higher Cr (III) ions concentrations, the available sites of adsorption become fewer, and hence the percentage removal of Cr (III) ions decreases [Yu *et al.,* 2003].

4.4 Effect of Initial Metal ion Concentration.

It is evident from Fig. 4(b) that, Cr (III) ions removal efficiency decreases with the increase in initial Cr (III) ions concentration. In case of lower Cr (III) ions concentrations, the ratio of the initial number of moles of Cr (III) ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, when the Cr (III) ions concentration is sufficiently large, the adsorbent's surface got occupied and the efficiency starts to decrease and the molecules desorbed from the adsorbent's surface. At higher Cr (III) ions concentrations, the available sites of adsorption become fewer, and hence the percentage removal of Cr (III) ions decreases [Yu et al., 2003].

4.5 Effect of contact time

From Fig. 4(c), it is evident that, Cr (III) ions uptake does not follow any regular pattern. This may be due to the available free spaces for adsorption. In this experiment, adsorption rate initially was increased rapidly, and the removal efficiency was reached at maximum (84.6%) within about 6 hours.

4.6 Effect of Biosorbent dose

The efficiency for the removal of Cr (III) ions increases with increase in the biosorbent dose as evident from Fig. 4(d), This is because the increase in the biosorbent dose results in more contact surface of adsorbent particles and therefore increase in availability of more binding sites for adsorption process [Garg, U. K., 2004].

4.7 Effect of Temperature

The temperature has two major effects on the adsorption process. One of them is that rising temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbent particles. This is because liquid viscosity decreases as temperature increases. Generally speaking, the effect of temperature on the adsorption rate constants in liquid-solid sorption systems is likely a complicated issue. Literatures have reported many cases in which the increase in temperature caused a decrease in the rate constants of different adsorbate ions [Horsfall and Spiff, 2005]. From a physicochemical perspective that is based on the behaviour of gases, the rate constant is expected to usually increase as the temperature is increased [Rosene and Manes, 1977]. This is usually caused by the fact that the increase in temperature, in a medium where the intermolecular forces are very weak, leads to an increase in the kinetic energy of gas molecules or atoms and thus enhances the rate of reactions.

4.7 The Thermodynamics

The data obtained for the thermodynamics parameters (Table 3) shows that the adsorption of Cr (III) ions unto the groundnut husk is an endothermic process as evident from the positive value of ΔH^o. Similarly, the positive value of ΔS^o results in a negative values for the ΔG^o of the adsorption process at the experimental temperature range (298 – 333 K). This indicates that the biosorption of Cr (III) ions by groundnut husk is feasible and spontaneous in nature at these temperatures.

5. CONCLUSION

This study presents groundnut husk as low-cost adsorbent for effective removal of Cr (III) ions from aqueous solutions. The removal efficiency was found to be dependent on the initial Cr (III) ions concentration, temperature, biosorbent dose and contact time at optimum pH of 4. The isotherm data was analyzed by the Langmuir, Freundlich, Temkin and BET isotherms and the data fitted BET model than others. The kinetic of the biosorption process of the metal ions was best described by a pseudo-second order.

Thermodynamics investigation showed that standard Gibb's free energy change (ΔG^o) was negative (for example, -24.4 kJmol^{-1} at 298 K) indicating that the biosorption of Cr (III) ions by groundnut husk is feasible and spontaneous in nature at some temperature studied. The standard enthalpy change (ΔH^o) with a value of +32.2 kJ/mol implies that the reaction was endothermic and non-physical in nature while +81.9 kJ/molK^{-1} value of standard entropy change (ΔS^o) implies an irregular increase in the randomness at the solid/solution interface of the biosorbent during the biosorption process. The comparison of the results obtained in this work to those reported in the literature for various agricultural waste biosorbents showed that groundnut husk biomass was an efficient biosorbent for the removal of Cr (III) ions from aqueous solution.

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COMPETING INTERESTS

Authors declare that no competing interests exist.

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