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Adsorptive Removal of Chromium from Tannery Wastewater by Chitosan Modified-Activated Carbon of *Hyphaene Thebaica*

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ABSTRACT

The continuous decline of freshwater resources has necessitated the quest for the treatment of wastewater. Consequently, an adsorptive method of removal of major pollutant (chromium) of tannery wastewater was initiated using chitosan-modified activated carbon derived from shells of *Hyphaene thebaica*. The activated carbon was initially synthesized by carbonization in an inert environment and chemically activated with 1.0 M Zinc Chloride ($ZnCl_2$) solution. The surfaces of both the native and chitosan-modified-activated carbons were characterized by X-ray diffraction, Brunauer Emmett Teller (BET) surface analysis, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The materials were also evaluated for Chromium (Cr) ions removal bybatch adsorption experiment. High adsorption efficiency (97.2%) was observed using chitosan-modified-activated carbon, which was largely influenced by facile modification of the material which subsequently led to the effective synergy between chitosan and the derived activated carbon. The batch adsorption of Cr ions revealed a dependence on adsorbate concentration (11.5 mg/L), adsorbent dose (0.8 g/ 100 mL), contact time (90 mins) and pH (4) with high adsorption efficiencies at optimum levels of such operating parameters.The equilibrium adsorption data are well described by the Freundlich model while kinetics data are favourably defined by the pseudo-second-order model for both chitosan-modified and native activated carbons. In the context of its environment-friendliness and abundance in the Sudano-Sahelian region of Africa, activated carbon derived from shells of *Hyphaene thebaica* and modified with chitosan demonstrated practical application in the removal of the environmentally deleterious level of Cr ions from real tannery wastewater with high adsorption efficiency of 97.2%, regardless of the presence of other competing heavy metal ions, tested at optimum operating parameters. Hence, when the surface of activated carbon derived from *Hyphaene thebaica* is properly engineered could be a material of great value for industrial wastewater treatment of metal ions.

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1. Introduction

Treatment of industrial wastewater in connection to the removal of heavy metal ions for pollution abatement and recovery of water has attracted great attention. This is owing to the importance of water— one of the necessities of life. Water supports life by sustaining both humans', animals' and plants' exterior and interior physical and biochemical processes. However, due to ever-rising environmental pollution stresses, water contamination causes freshwater insufficiency and thus its availability declines incessantly regardless of the destruction of natural water-supporting systems [1]. One serious environmental burden is heavy metals and water contamination. Heavy metals like

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chromium, cadmium, lead and anionic arsenic are major underground water contaminants worldwide and are hazardous to human health [2]. Of great environmental concern, chromium could be present above the threshold limit in water bodies, as the metal is widely used in many industrial operations such as electroplating, leather tanning, and textile industries, that generates a large volume of wastewater compromising environmental quality and human health [1,2]. Due to the scarcity of freshwater occasioned by the rapid rise of urbanization and ravaging climatic change, the reclamation of wastewater could be an alternative option and buffer for water supply. At the same time, in the years coming, the effort will diminish the water pollution problem.

To address this problem, various treatment technologies for the removal of heavy metals from industrial wastewater by sequestration through numerous separation techniques including ion exchange, membrane filtration, nanofiltration, selective precipitation, chemical precipitation, photocatalysis, and adsorption are applied[1]. To avoid a suboptimal choice or the failure of wastewater reclamation activity,the selection of either of these methods deserves extensive treatment system performance evaluation and attention [1,3]. In general, adsorption-based technologies are easy-to-handle and have proven very promising among the most viable options proposed for the treatment of industrial wastewater contaminated by a wide spectrum of pollutants covering both organic and inorganic. More so, the cost of coagulants (like aluminium sulphate), ion exchange resins (like polystyrene sulfonate), membranes (like cellulose acetate) and photocatalysts are much higher than simple adsorbents like activated carbon used for adsorption. Therefore, the general acceptability of adsorption technique lies on its low processing and instrumentation costs (as it involves simple design), ease of operation, multitude availability of low-cost and environment-friendly adsorbents that are easily regenerated and fast separation ability, little or no generation of harmful by-products accompanied by high-efficient removal of wastes [4,5,6].

Although wide varieties of adsorbents sourced from myriads of materials, namely biomass, natural and modified clays, metal oxides, carbon nanotubes, and polymers have been successfully applied in aqueous solutions for the removal of heavy metals [7,8]. However, it will be of great interest if very low-cost adsorbent materials could be sourced from animals and plants, which their disposal is either a waste of resources or a source of environmental nuisance. To avoid such, the decomposable waste of plants and animals which are thrown into the environment can be harnessed and used to produce value-added bio-material which in turn reduces the production of wastes with a double advantage of environmental cleanliness and resource utilization, which would ultimately encourage operational guidelines of Circular Economy and the "near-zero discharge" of waste [9].

In line with the principles of no material is of zero-value and Circular Economy, very promising and inexpensive materials are many abound including chitosan. It has been reported that chitosan has a high potential for the adsorption of metal ions [1]. This is because of its biophysical and chemical properties such as hydrophobicity, biocompatibility, biodegradability, non-toxicity and the presence of very reactive amino (—NH_2) and hydroxyl (—OH) groups in its backbone, which attracts chitosan as an effective adsorbent material with a pool of chelation sites suitable for sequestration of metal ions and other cocktails of water pollutants [10]. However, the major drawbacks of native chitosan are dissolution in acids normally caused by high charge density on its positively charged polymeric framework, and *in-situ* cross-linkage between branched chain polymers in water, which ultimately causes low surface area of the material [10]. In addition, native chitosan is insoluble in water or organic solvents but becomes soluble when the pH of an aqueous solution is below 5 [11,12,13]. In response to these drawbacks, different surface and framework modifications of chitosan were fabricated with different materials including activated clay, montmorillonite, bentonite, zeolites, polyurethane, oil palm ash, calcium alginate, polyvinyl alcohol, cellulose, magnetite, sand, cotton fibres, perlite and ceramic alumina have been used to improve its both mechanical/physical and chemical stability in an aqueous environment [14,15,16,17,18]. Nevertheless, in an attempt to make full

utilization of bio-resources around us, shells of *Hyphaene thebaica* are found in a wide area of the Sahelo-Sudanian region of Africa. It is one of the commonest species of *Arecaceae* [19, 20]. By impression, the shell of *Hyphaene thebaica* has been identified as a very hardened ligneous material by the native people in the region. All the same, it is worth mentioning that lignin in plant-based materials is the key component responsible for adsorption [21,22,23]. Despite this advantage, the shells of this plant have been thrown as wastes and therefore, its prospect for use as activated carbon for supportive modification of an animal-based adsorbent such as chitosan is lacking.

Hence, the novelty of the present work is the application of chitosan-modified activated carbon of shells of *Hyphaene thebaica* for the removal of chromium ions from tannery wastewater, prepared by the impregnation method. The primary aim here is to enhance the adsorption performance of chitosan and activated carbon of *Hyphaene thebaica* by the combined effect of the two following increased chemical stability, mechanical strength, and surface adsorption sites. This system is notably unexplored for the adsorptive removal of chromium from an aqueous environment.

Despite that chromium can exist in either of Cr (III) in cationic form (e.g., Cr^{3+}) and/or Cr (VI) in anionic forms (e.g., $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and $HCrO_7^-$) in the environment, its other oxidation states are not stable in aerated aqueous media [24]. Because of its detrimental effects on biological systems, considerable studies on the removal of chromium from an aqueous environment by the adsorption process are many abound. Herein, this research reports the removal of chromium ions from tannery wastewater using chitosan-modified-activated carbon of shells of *Hyphaene thebaica*. Also, the adsorption performance of the prepared material was comprehensively investigated using different adsorption isotherm and kinetics models.

2.0 Materials and methods

2.1 Materials and Reagents

The precursory material used in this study for the synthesis of activated carbon was shells of *Hyphaene thebaica*, which was used to modify the adsorptive characteristics of chitosan. The natural shells of *Hyphaene thebaica* were obtained from the Northern part of Bauchi State, Nigeria, the Sahelian sphere of the State and where the plant is widely distributed. The shells were dried, washed and rinsed thoroughly with water. The shells were then broken to remove the inner contained nuts.

The commercially-based chitosan was directly purchased from Aldrich and used as supplied. All chemicals of analytical grade were purchased from Aldrich including $ZnCl_2$, $K_2Cr_2O_7$, NaOH, HNO_3,and HCl. The salt of $K_2Cr_2O_7$ was used for the preparation of aqueous solutions of varied concentrations with deionized water (Millipore Milli-Q Merck) meant for adsorption tests and where pH adjustment was needed, a few drops of HCl and NaOH solutions were used. The $K_2Cr_2O_7$ was selected for the simulation experiment because of its higher solubility and bioavailability as well as being more toxic even at a low concentration than Cr (III) (which forms stable cationic complexes from 80 to 90 % of its species present in tannery wastewater) [25].

The tannery wastewater samples were collected in acid-washed and deionized water-rinsed containers from the point of effluence of the Hide & Skin processing company (tannery) in the industrial layout of Kano State, Nigeria. The collected wastewater samples were acidified with concentrated HNO_3 and then transported in a cool box stocked with ice blocks to the laboratory where all the samples were stored at 4 °C under refrigeration before analysis.

2.2 Production of activated carbon

The activated carbon in this research work was produced following the method reported by Tan et al. (2008) [26] with slight modifications. The shells of *Hyphaene thebaica* were thoroughly washed with tap water to free dirt and dust attached to the surface of the materials. The shells were then rinsed thoroughly with deionized water. The washed shells were dried in an oven (FC-1000 Blast) at 105 °C for 4 hrs and then crushed with a pestle and mortar to the convenient size of approximately 2mm. 1000 g of the crushed sample of the plant was carbonized in a muffle furnace (Model: Banstead, 1A USA) at 500 °C for 15 min. The carbonized sample was soaked in 1.0 M $ZnCl_2$ at a solid-to-solvent ratio of 1:3 for 24

hrs and subsequently activated at 500 °C for another 15 min [27]. Thereafter, the sample was taken out of the muffle furnace and allowed to cool in a standard-type desiccator (φ 215mm). The cold sample was then severally washed with deionized water until a pH range of 6 to 7 was achieved. The obtained adsorbent from the shells of *Hyphaene thebaica* was then oven-dried at 105 °C for 24 hrs.

2.3 Preparation of chitosan gel and modification

A measured 5 g of commercially based chitosan was slowly added to 100ml of 10 % (w/v) oxalic acid while constantly being stirred in a beaker. The content of the beaker was heated to 50 °C to facilitate homogeneity in mixing. Thereafter, a whitish viscous mixture of chitosan-oxalic acid was obtained, which was used for the modification with activated carbon of shells of *Hyphaene thebaica*following the procedure described in the literature [28].

As presented in the chitosan structural presentation below, the reactive groups found in chitosan are a primary amino group (C2) and primary and secondary hydroxyl groups (C6, C3). Glycosidic bonds and the acetamide group can also be considered functional groups. These functional groups allow for a great number of chemical modifications, producing the materials with new properties and behaviours.

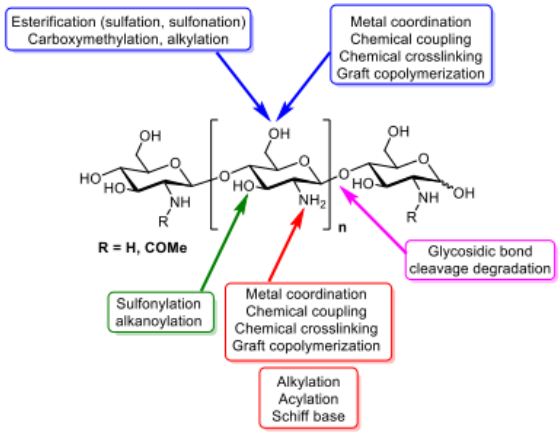

Figure 1. Presentation of surface functional groups that can be chemically modified.

From the obtained chitosan gel, 100 mL was measured and diluted with 500 mL of deionized water, followed by heating to 50 °C. A measured 50 g of the activated carbon produced from shells of *Hyphaene thebaica* was added to the diluted chitosan gel in a container and mechanically agitated by a shaker at 70 osc/min for 24 hrs. The prepared chitosan-coated activated carbon was thoroughly washed with distilled water, dried and followed by 3 hrs soaking in 0.5 % NaOH solution. The excess NaOH solution was decanted out while the residues left were rinsed thoroughly using deionized water and subsequently, oven dried at 105 °C, allowed to cool under room temperature and stored in a desiccator [28].

2.4 Physico-chemical analysis of tannery wastewater

The tannery wastewater samples collected from the discharge point to drain wastewater were subjected to analytical measurements. The analytical parameters considered herein are pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), turbidity, dissolved oxygen (DO), biological

oxygen demand (BOD_5), chemical oxygen demand (COD), and the environmentally concerned heavy metal ions of cadmium (Cd), chromium (Cr), nickel (Ni) and lead (Pb). Temperature, pH and electrical conductivity (EC) values were determined onsite by a three-in-one portable digital temperature/pH/EC meter (Temp/pH/EC-983). Similarly, dissolved oxygen content (DO) was also determined onsite with a waterproof digital DO meter. The TDS was measured gravimetrically following the standard methods described by APHA [29]. The BOD in 5 days normally written as BOD_5 conducted at 20 °C and COD were all measured following standard methods [30].

For heavy metal analysis, the wastewater sample was digested as follows. A measured 100 mL of the tannery wastewater was transferred into a beaker, followed by acidification using 5 mL of concentrated HNO_3 along with the addition of a few boiling chips. The content in the beaker was then heated on a hot plate, which was allowed to boil and evaporate until the volume was reduced to 20 mL. The heating and addition of concentrated HNO_3 were continued until the solution became clear. The wall of the beaker was rinsed with deionized water, followed by filtration. The filtrate was transferred into a 50 mL volumetric flask and the volume was adjusted up to a mark with deionized water, which was then thoroughly homogenized before atomic absorption spectrophotometric (AAS) analysis [31]. The determination of the concentration of chromium and other heavy metal ions in the wastewater sample was carried out instrumentally with AAS (Model: Analyst 200, Perkin Elmer). However, it is worth mentioning that chromium was the metal given preference here in this study and its initially determined concentration in the wastewater sample was used as the baseline concentration for all the subsequent adsorption experiments.

2.5 Characterization of Adsorbent

To understand the surface characteristics of the prepared adsorbents, a small quantity of both native material (derived activated carbon) and chitosan-modified were subjected to surface characterization. The surface morphology of both native activated carbon and chitosan-modified activated carbon was captured with Scanning Electron Microscope (SEM)(Model: Phenom ProX, MVE 1329F). The surface area of the prepared adsorbent materials was determined by the N_2 adsorption/desorption method using the BET surface area analyser. For the detection of surface functional groups present in both native and the prepared chitosan-modified activated carbons, Jasco IR 4100 spectrometer (Japan) was used.

2.6 Adsorption tests

The adsorption characteristics of both native activated carbon of *Hyphaene thebaica*and chitosan-modified-activated carbon of *Hyphaene thebaica* for chromium removal in simulated chromium wastewater (chromium spiked solution) and in the real tannery wastewater solution were tested in a batch experimental mode. For the simulated tannery wastewater, the adsorption tests were conducted at room temperature and without pH adjustment. The tests were conducted using five (5) different dosages of the prepared adsorbents (0.4 g, 0.8 g, 1.2 g, 1.6 g and 2.0 g) with 100 mL of each of the real tannery wastewater and chromium spiked solutions in a corked 250 mL conical flask. The conical flask containing the mixture was agitated with the aid of a mechanical shaker (RJH-5005 digital) at a constant speed of 70 Osc/minute to ensure homogeneous mixing and attainment of equilibrium. The flask containing the mixture was withdrawn from the shaker after the predetermined time intervals (30, 60, 90, 120 and 150 min), filtered with Whatman filter paper and the residual concentration of the chromium ion left was measured using AAS.

To determine the uptake of chromium ions over the tested adsorbents, the mass uptake of chromium per unit mass of the prepared adsorbents (mg/g) was calculated using equation (1):

$$qe = \frac{(Co - Ce)V}{m} \qquad (1)$$

where q_e is the number of chromium ions adsorbedat equilibrium by the adsorbent (mg/g), C_i is the chromium initial concentration (mg/L), $C_e$is the solution equilibrium concentration (mg/L), V is the volume of the solution (L) and m is the mass of adsorbent used (g) [32].

However, to determine the percentage removal of chromium ions from the solutions, the amount was determined from the difference between chromium ions adsorbed and that

remained in the solution [33]. The efficiency (R) of removal of chromium ions from the tannery wastewater was determined based on the following equation (2):

$$R = \frac{(Co - Cf)}{Co} X100 \quad (2)$$

where C_o and C_f are the initial and final concentrations of the chromium ions in the solution (mg/L) [34].

The effect of contact time in relation to the adsorption capacity of the prepared adsorbent materials was investigated at fixed time intervals of 30—150 mins. The adsorption experiments were conducted with varied initial chromium concentrations (C_0 = 0.50–11.50 mg/L), which were chosen based on the range between maximum concentration found in the tannery wastewater and maximum tolerable limits in accordance with USEPA and WHO standards. Similarly, the effect of different dosages of the adsorbent materials (0.4–2.0 g) was tested in separate conical flasks containing 100 mL of wastewater containing chromium, covered and agitated with aid of a mechanical shaker. For the experiments on the effect of pH, the experimental solutions containing chromium ions were initially adjusted with aqueous solutions of 0.1 M HCl or 0.1 M NaOH to reach pH values between 4 and 9. For all the tests carried out for various factors affecting the adsorption of chromium ions, the experiments were conducted in separate conical flasks each with 100 mL of simulated chromium wastewater (chromium spiked solution), executed at a contact time of 2 h 30 min at a speed of 70 osc/min and at a room temperature. The residual concentrations of chromium were all determined with AAS.

In addition, the adsorption experiment of chromium in presence of coexisting heavy metal ions in the real tannery wastewater was conducted at optimum operational conditions predetermined with simulated chromium wastewater, where filtrates were analysed by AAS to determine residual concentrations of Cr ions and other competing heavy metal ions.

2.7 Adsorption isotherms

The adsorption behaviour of chromium ions over the prepared adsorbents was tested by Langmuir and Freundlich isotherm models. The mathematical linear form of the Langmuir adsorption isotherm model is given in Equations (3).

$$\frac{Ce}{Qe} = \frac{1}{qmKL} + \frac{Ce}{qm} \quad (3)$$

where *Ce*, is the equilibrium metal concentration,*and* $q_m$and K_L are the Langmuir constants defined as the maximum adsorption capacity (mg/g) and relative energy of adsorption (L/mg), respectively. A graph of *Ce/qe* against *Ce* gives a linear plot with a slope of *1/qm* and an intercept of $1/qmK_L$[35].

Similarly, another important dimensionless parameter, separation factor, R_L, that further characterizes the Langmuir equation was also calculated, which is defined as in equation (4) below:

$$R_L = \frac{1}{[1+(KlCo)]} \quad (4)$$

where C_0 is the highest initial chromium ion (mg/L). R_L describes the shape of Langmuir isotherm, where adsorption is unfavourable if $R_L > 1$, favourable if $0 < R_L < 1$, irreversible if $R_L = 0$, and linear if $R_L = 1$ [36].

However, the Freundlich adsorption isotherm model characterizes heterogeneous surfaces comprised of multilayer adsorption surfaces. The mathematical linear forms of the adsorption isotherm model are given in Equation (5):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where ***qe*** is the number of metal ions adsorbed per unit mass of adsorbent (mg/g), *Ce* is the equilibrium concentration of the adsorbate (mg/L), K_f and n are Freundlich equilibrium constants [37], which can be obtained from the linear plot of *lnqe* against *lnCe*. The linear plot gives a slope of *1/n* while an intercept is lnK_f.

2.8 Adsorption Kinetics

The adsorption kinetics of chromium was carried out with 0.8 g of the prepared adsorbents (native and chitosan-modified activated carbons) in separate flasks containing 100 ml of 11.50 mg/L of chromium solution at pH 4.0. The contents of the flasks were agitated at a speed of 70 osc/min and the concentrations of the

solutions were monitored at time intervals of periods beginning from 30 to 150 mins at room temperature. After each of the time intervals, filtrations were carried out and the filtrates were analysed by AAS. The chromium uptake capacity over the adsorbents, *qt*, was calculated at every time interval, *t* (min), using Equation (6).

$$q_t = \frac{(C_0 - C_t)\mathrm{V}}{m} \quad (6)$$

where *qt* is the amount of adsorbate adsorbed at time t per unit mass of the adsorbent (mg/g), $C_0$is the initial chromium concentration (mg/L) at zero time, and C_t is the chromium concentration (mg/L) in the solution at time t [38]. The kinetics experimental data was tested for Pseudo-first and-second order models, which were used to determine the rate and mechanism of interactions between adsorbate (chromium ions) and adsorbents.

The kinetic models employed in this adsorption process over the adsorbents were the most commonly applied kinetics models, namely the Pseudo-first and-second order models, as well as the intra-particle diffusion model, which was applied to describe the kinetics data in relation to the kinetic mechanism that controls the chromium adsorption process. The mathematical linear form of the Pseudo-first order kinetics model is presented in Equation (7) while the expression of the Pseudo-second order kinetics model is presented in Equation (8).

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where *qe* (mg/g) is the amount adsorbed at equilibrium, *qt* (mg/g) is the amount adsorbed at time *t*, whereas k_1(min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants for Pseudo-first and Pseudo-second order kinetics models, respectively [39].

However, for the intra-particle diffusion model, the model is described by Equation (9):

$$q_t = k_{id} t^{1/2} \quad (9)$$

where $\boldsymbol{k_{id}}$ (mg/g min$^{1/2}$) is the rate constant, which can be determined from the slope of a plot of $\boldsymbol{q_t}$ against $\boldsymbol{t^{1/2}}$[40].

3.0 Results and Discussion

3.1 Physicochemical Parameters of Tannery wastewater

The physicochemical analysis of the tannery wastewater sample revealed that the tannery effluent is dark brown, slightly alkaline, and highly turbid with a lot of dissolved and suspended solutes. The effluent has a pungent smell, high electrical conductivity and high chemical oxygen demand. Further analysis revealed the presence of chromium and other metal pollutants of environmental concern. These parameters are given in Table 1.

The high turbidity of the tannery effluent characterised by dark brown colour indicated that the wastewater contained highly coloured compounds that are significantly detrimental to the aquatic environment. The environmental impact associated with high turbidity/colour is its ability to inhibit penetration of sunlight and causes deceleration in the rate of oxidation of the pollutants in the water regime. A similar observation was made in the effluent of a tannery in Zaria, which was characterised bya dark-brown appearance with an unpleasant odour [41].

The higher value of pH shows that tannery wastewater was alkaline in nature, which might be caused by the high presence of carbonates and bicarbonate. The high-pH tannery effluent discharged into the nearby water channels may cause fluctuation of the pH of the water body, which may affect the chemistry of the water body that could be detrimental to aquatic plants and microorganisms. The basic nature of the tannery effluent may be attributed to the high utilisation of salts by tanneries in their operational tanning process. The presence of carbonates and bicarbonates in the effluent may cause significant retardation of natural attenuation or degradation of water contaminants, particularly organics due to buffering effect of the carbonates. The electrical conductivity (EC) level of the tannery wastewater was beyond the standard limit. The EC of the tannery wastewater indicated a high level of salts in the effluent. The elevated level of EC in wastewater is mainly attributed to the presence of Cl^- ions and inorganic salts of Na^+, K^+, $Ca^{2+}$and Fe^{3+} that create more salinity in water [42], which indicates that there was a high discharge of inorganic chemicals as cations and anions into receiving water body. The implication of high EC in the water environment, though lies in the chelating properties of the water body, it creates an imbalance of metal bioavailability for uptake by

both aquatic flora and fauna [43, 44]. In addition, when untreated and/or partially treated tannery effluent with high salt content is directly discharged into a water course, there could be resultant stresses on the soil environment if the water of the receiving body is used for irrigation.

Although the TDS of the tannery effluent was within the permissible limits of both USEPA and WHO, the TDS in the effluent sample could be mainly caused by the presence of carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, calcium, sodium, and potassium in the chemical inputs used in the processing of hides and skin. However, since TDS is the measure of total inorganic salts and other dissolved substances in the tannery effluent, discharge of tannery effluent with high concentrations of sulphates, nitrates, and phosphate into a watercourse (e.g., river) could support the eutrophication process in the receiving water course. This could affect or limit the self-purification capacity of tannery effluents receiving water bodies [45].

The low dissolved oxygen (DO) in the effluents might be due to the high demand for oxygen in the bio-oxidation of organic pollutants by microorganisms in the tannery wastewater. This means that the presence of organic contents in tannery wastewater causes an increase in microbial activity that consumes or depletes dissolved oxygen in their biological activity of decomposing organic matter, which creates stresses on aquatic organisms. Therefore, the discharged tannery effluent was heavily polluted and thus, is potentially highly deleterious to aquatic living systems. In addition, by the nature of the values of BOD and COD of the tannery effluent, the wastewater could affect aquatic ecosystems receiving water courses of the effluent. Because BOD defines microbial oxygen demand that causes depletion of DO, the attendant consequence is hypoxia conditions which exacerbate life for aquatic biota. The main environmental problem of BOD is the encouragement of anaerobic activity, which leads to the release of noxious gases such as ammonia (NH_3), hydrogen sulphide (H_2S) and organic acids (acetic acids and butyric acid) in water ecosystems [46]. However, the increased COD could result from the presence of some organic compounds in the effluent, which are non-biodegradable and as result resist bacterial decomposition [47].

Other major heavy metal ions found in the tannery wastewater were cadmium (Cd), chromium (Cr), nickel (Ni), and lead (Pb). The measured concentrations of the metal ions in the tannery wastewater exceeded the threshold limits set both by the world health organization (WHO) and the united state environmental protection agency (USEPA). However, the level of Cr was found to be the highest among the five detected toxic elements in the tannery effluent, which was caused by pickling and chrome-tanning processes. This resulted from the high usage of chromium salts in the chrome-tanning process. As a result, the tannery effluent could impose severe problems in the ecosystems of the receiving natural water resources around the industry. Moreover, the fact that the concentration of Cr in the tannery effluent was 230 times the threshold limit and was discharged into the open common drain without any thought of environmental concern, the pollutant could ultimately make its way into the major water courses around such as rivers and subsequently percolates down to the underground water. Consequently, the situation becomes not only an emerging environmental nuisance but also a societal challenge since it could hardly be managed and controlled once the such situation is established. And this would ultimately pose a serious threat to aquatic living systems and affects the routine as well as the functional aquatic ecosystem services. Hence, for pollution management and protection of the fragile environment especially the natural freshwater resources, effective removal of Cr from the source point is non-negotiable.

Table 1. Physico-chemical characteristics of tannery wastewater

Parameters	Tannery sample	WHO Standard	US EPA Standard
Turbidity (NTU)	943.000	-	-
pH	8.700	6.00-9.000	6.00-9.000
EC (µs/cm)	6,470.000	-	2,500.000
TDS (mg/L)	952.000	1,500.000	2,000.000
DO (mg/L)	0.570	>1.000	-
COD (mg/L)	181.710	150.000	250.000
BOD_5 (mg/L)	23.400	30.000	50.000
Cr (mg/L)	11.500	0.050	0.050
Ni (mg/L)	0.810	0.020	0.200
Pb (mg/L)	0.640	0.010	0.006
Cd (mg/L)	0.920	0.003	0.010

3.2 Surface Characteristics and Chemistry of the Adsorbents

To understand the surface characteristics responsible for the high efficiency of adsorption by chitosan-modified activated carbon of *Hyphaene thebaica* and unmodified activated carbon, Brunauer-Emmett-Teller (BET) using N_2adsorption–desorption experiments were conducted. The specific surface area, average pore diameter and pore volume are presented in Table 2. A marked difference in porosity between chitosan-modified activated carbon and unmodified activated carbon was readily observed. From the results of the N_2adsorption–desorption experiments, it is obvious that the noticeable high adsorption capacity of the chitosan-modified activated carbon compared to the unmodified activated carbon was surface area-driven (Table 2). In support of the above observation, the pore size distribution was characterized by the Barrett–Joyner–Halenda (BJH) method and the result is shown in Table 2. The chitosan-modified activated carbon showed the highest average pore volume corresponding with low average pore diameter compared to the unmodified activated carbon. Generally, adsorbents have different pore size distributions depending on the activation and modification methods [48]. Fundamentally, the International Union of Pure and Applied Chemistry (IUPAC) has categorized pore diameters into different classes of ≤2, 2–50 and ≥50 nm for micropores, mesopores and macropores, respectively [48]. From Table 2, the unmodified activated carbon predominantly consists of mesopores while the pore types in chitosan-modified activated carbon are mainly made up of micropores (Table 2). The microporosity of the chitosan-modified activated carbon might result from the blockage effect of chitosan particles, which presumably entered into the formed mesopores of the material and changed the pore type into micropores after the modification. The predominant concentration of micropore structure in the chitosan-modified activated carbon indicates the available surface area, which is advantageous to the adsorption process. To corroborate this view, the surface area of the material stands at 941 m^2/g, which falls within the standard range of 500—1,500 m^2/g for commercial activated carbon [48]. This observation was also reported in a similar study where the average pore diameter of prepared activated carbon was initially 2.47 nm (mesoporous) and subsequently changed to 1.27 nm (microporous) after modification with chitosan [49].

Table 2. Surface properties of Chitosan modified Hyphaene thebaica adsorbent.

Surface property	Adsorbents	
	Unmodified activated carbon of *Hyphaene thebaica*	Chitosan modified-activated carbon of *Hyphaene thebaica*
BET surface area (m^2/g)	779.000	941.000
Pore volume (cm^3/g)	0.220	0.710
Average pore diameter (Å)	20.150	4.900

Fig. 2 presents the micrographs of the surface morphological characteristics of both the unmodified and chitosan-modified activated carbon produced from shells of *Hyphaene thebaica* were taken at a Field of View (FOV) 537 µm and magnification of X1000. The surface of both modified and unmodified adsorbents shows a series of pores that are polygonal in shape. This could be attributed to the activation influence of zinc chloride that can penetrate deeply into the internal structural matrix of the adsorbent precursors to create pores internally [27]. Therefore, the number, size and shape of the pores on the adsorbents are the determinants of the physical adsorption of metals by the adsorbents.

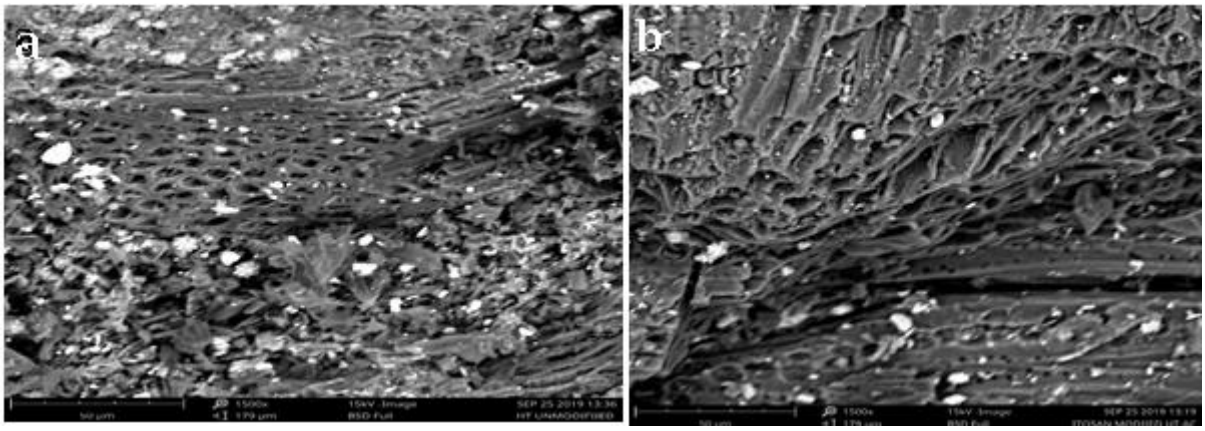

Figure 2.SEM morphological image of (a) activated carbon of *Hyphaene thebaica* and (b) chitosan modified-activated carbon of *Hyphaene thebaica*.

The surface chemical characteristics of the adsorbent materials were determined by

FTIR spectral analysis for both chitosan-modified activated carbon and unmodified sample in order to decipher the partaking of functional groups in the adsorption process. In the FTIR spectra of activated carbon of *Hyphaene thebaica*, the peaks demonstrated at 1684 cm^{-1} and 1561 cm^{-1} present stretching vibrations of C=O in carbonyl and carboxylic groups and stretching of C–O and O–H distortion in carboxylic acids, respectively [50, 51]. The vibrational peaks at 1478–1606 cm^{-1} in the FTIR spectra of the chitosan-modified-activated carbon of *Hyphaene thebaica* are peaks specifically assigned to N–H scissoring from the amines and amides [44]. In addition, the peaks at 1561 cm^{-1} in the spectrum of unmodified activated are noticeably broadened and changed to 1606 cm^{-1}after modification of the material with chitosan, which may be attributed to the interaction between the two materials. Therefore, the appearance of such peaks confirmed that chitosan was successfully anchored on the activated carbon of *Hyphaene thebaica*. Consequently, the chitosan modified-activated carbon has superior surface chemical properties or functionalities and thus, resulted in better adsorptive removal of chromium because of the added advantage of the appearance of the peak of N–H scissoring from the amine and amide functional groups that can interact with Cr ions both through hydrogen and electrostatic attractions. This is not surprising since the biopolymer nature of chitosan has a combined high density of both hydroxyl (–OH) and primary

amine (–NH_2) groups which can serve as additional active adsorption sites [52] and thus, making the chitosan-modified activated carbon of *Hyphaene thebaica* an efficient adsorbentwith superior adsorption capacity than the unmodified activated carbon of *Hyphaene thebaica*. Unlike the unmodified activated carbon that is abundant in carbon, hydrogen and oxygen, chitosan-modified-activated carbon contained additional nitrogen, making it more active in the adsorption process. It is this unique surface functionality that expands the adsorption potential of chitosan-modified-activated carbon. Because amine groups, for example, are nucleophilic and can strongly attract metal ions because of the presence of lone pairs of electrons on nitrogen atoms [53, 54]. In this context, coupling chitosan to the activated carbon of *Hyphaene thebaica* improved the affinity of the material to bind with positively charged ions. Therefore, amino groups present in the composite adsorbent material create a multitude of electron-rich sites, which can allow the adsorption of metal ions through electrostatic interactions.

From the FTIR peaks a and b provided in Fig. 3, it can be observed that the major peaks of interest in both spectra (3652.8 cm^{-1}) of modified and unmodified materials correspond to the absorption band of a non-bonded hydroxyl group (3645-3600 cm^{-1}) connoting the presence of alcohol and phenolic compounds. The peak detected at 3328.7 cm^{-1} designates the presence of primary amines group in the materials. The vibrational peak observed at 1364.2 cm^{-1} designates the presence of alkyl and nitro groups. However, the two peaks observed at 1852.5 cm^{-1} and 1561.8 cm^{-1} correspond to the absorption bands of carbonyl and secondary amine groups, respectively. These further confirmed that the adsorbents were made from the same source of the material. While the appearance of a sharp peak at 1315 cm^{-1} corresponding to amid III (C-N stretching) indicates the incorporation of chitosan onto the surface of the adsorbent material. This suggests additional active sites on the adsorbent material.

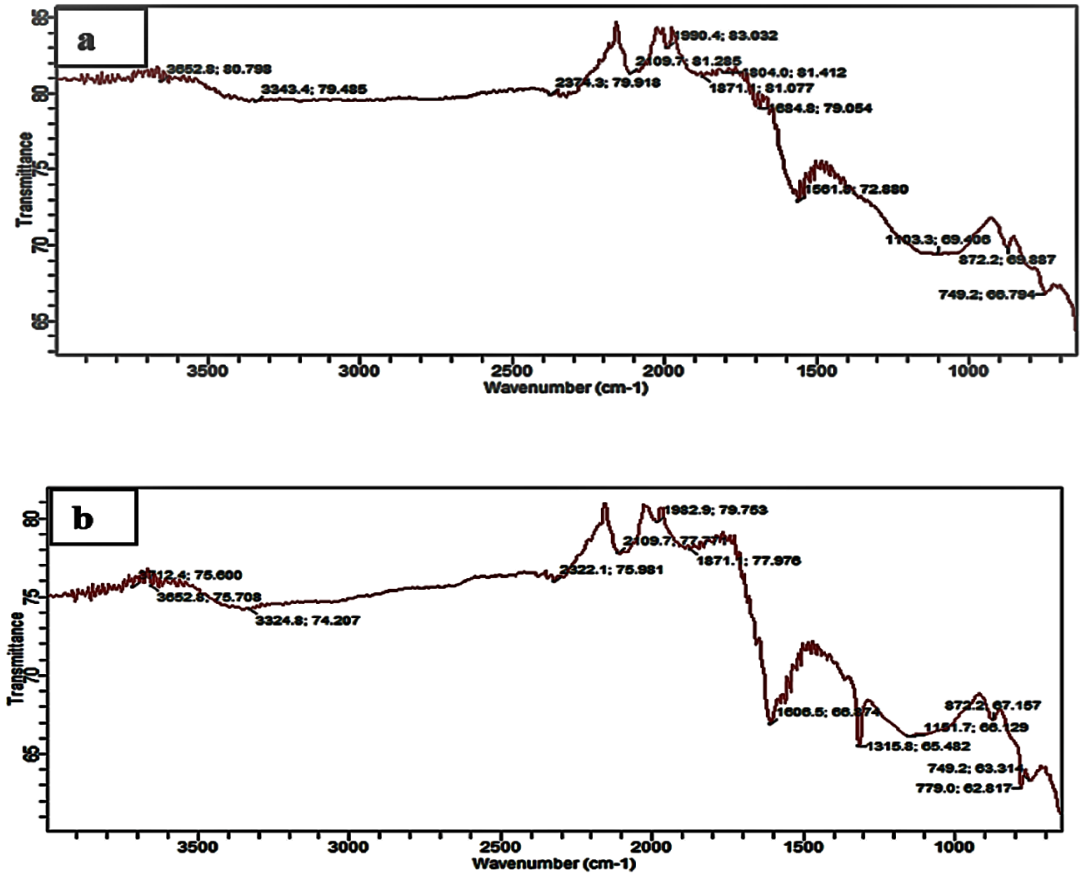

Figure 3. FTIR spectrum of (a) activated carbon of *Hyphaene thebaica* and (b) chitosan modified-activated carbon of *Hyphaene thebaica*.

3.3 Effect of contact time

Fundamentally, the efficiency of an adsorptive system largely depends on the time of adsorption and therefore, a study on the influence of contact time on the process is of significant importance. The performance characteristic of the adsorptive removal process of Cr ions by both chitosan-modified-activated carbon and unmodified activated carbon is presented in Figure 4. From the results illustrated in the Figure, the adsorption rate of Cr ions moved progressively in the beginning with an increase in percentage removal from 65 to 95 % as the contact time moved forward from 30 to 90 min. However, after 90 min, the rate of adsorption was in full swing decreasing slowly until the contact time reached 120 min corresponding to 94 % amount adsorbed. This could be attributed to the availability of enough vacant surface adsorption sites for the Cr ions. However, after an equilibrium time was reached, the number of available vacant sites became less which is generally true for adsorbents [55]. Hence, the maximum removal of 95 % of Cr ions was achieved at 90 min depicting the optimum time for the adsorption process. Thus, a further increase in time after 90 min was revealed to be of no significance. On the other hand, the progressive increase in the adsorption rate at the initial stage might be probably caused by a change in concentration gradient between the Cr ions in the solution and the number of available binding sites on the adsorbent surface initially. The decrease in the removal efficiency of Cr ions after an equilibrium state was reached may be caused by the limited mass transfer of Cr ions from the bulk liquid phase to the external surface of the adsorbent, which normally occurs in the adsorption process [56].

Similarly, the unmodified activated carbon powder followed the same trend of a performance characteristic of chitosan-modified-activated carbon powder. In its case, equilibrium time was also attained at 90 min with an adsorption capacity of 62 % and after which the rate of adsorption declined to 59 %. This further confirmed that the bulk of the materials used for the adsorptive removal of Cr ions from the solutions mainly originated and were made from the same source of material and thus, the dissimilarity observed in performance is caused by the modification.

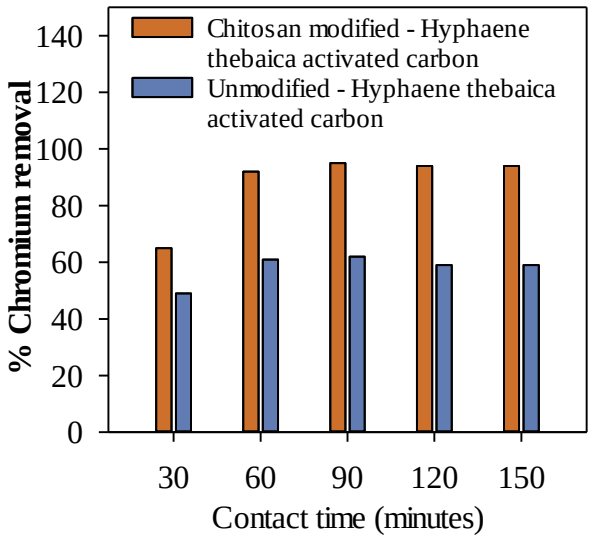

Figure 4. Effect of contact time on the adsorptive removal of chromium ions by chitosan-modified- and unmodified -activated carbon of *Hyphaene thebaica*.

3.4 Effect of initial metal concentration

The influence of initial chromium concentration on the adsorption process was studied by varying the initial concentration between 0.50 and 11.50 mg/L of the toxic metal used for the adsorption experiment, which was chosen based on the range between the maximum concentration found in the tannery wastewater and maximum tolerable limits in accordance with USEPA and WHO standards. The results are displayed in Figure 5. The Figure shows that the amount of Cr ions adsorbed increased proportionately with an increase in the initial concentration. It means that adsorption

efficiencies generally increased with the increase in the initial concentration until a point was reached where further increase in initial concentration yielded little or no commensurate improvement in adsorption efficiency. This may be attributed to the effect of an increasing concentration gradient that acted as the main driving force for the adsorption process and was impetuous enough to overcome adsorbate mass transfer resistance between the aqueous and solid phases [57] and as a result, was the responsible factor that also enhanced the interaction between the Cr ions and chitosan modified-activated carbon. In view of that, the initial chromium concentration was an important driving force responsible for overcoming the resistance of mass transfer of Cr ions between an aqueous phase and the chitosan-modified activated carbon. Generally, the effect of the initial concentration of adsorbate becomes exceedingly high and causes an increase in adsorption efficiency, which has been a universally observed trend in most similar studies [53, 54, 58].

On the aspect of unmodified activated carbon, the observed adsorption behaviour of the material followed a similar trend as in the case of chitosan-modified-activated carbon. It was only that the modification had initiated a variation in the maximum amount adsorbed as the concentration of Cr ions increased from 0.5 to 11.5 mg/L. In response, there was a corresponding difference in a rapid increase in adsorption efficiency from 76 to 95 % and 43 to 62 % for chitosan-modified and unmodified activated carbons, respectively. This means that there was a marked difference of more than 30 % adsorptive removal capacity between chitosan-modified and unmodified activated carbons, which is inferred to be an augmentation of several surface functional groups and binding sites for Cr ions caused by the chitosan matrix. Consequently, the adsorption performance of the modified-activated carbon surpassed the unmodified-activated carbon. However, overall, the results showed that the viability and efficiency of the adsorption process of the materials depend not only on the surface functionalities of the adsorbents but also on the concentrations of the chromium ions.

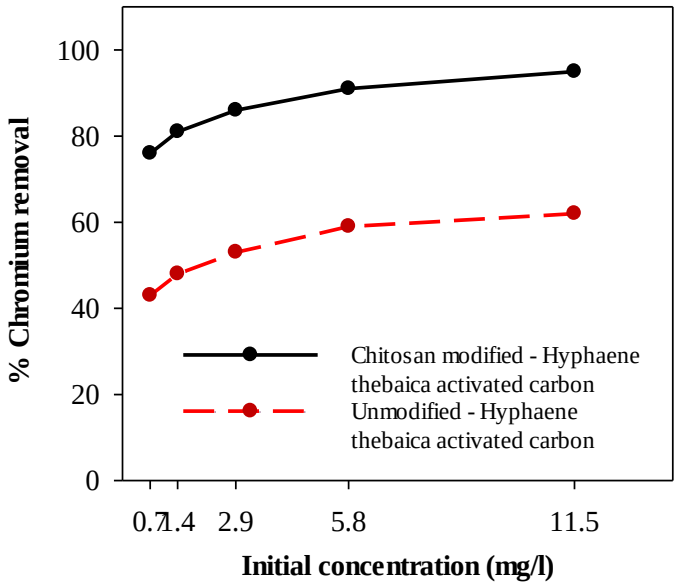

Figure 5. Effect of chromium initial concentration on the adsorption capacity of chitosanmodified and unmodified activated carbons of *Hyphaene thebaica*.

3.5 Effect of adsorbent dosage

Fig. 6 shows the effect of the dosage of adsorbent. It was observed that the increase in surface active sites was proportionate with the increase in the adsorbent dosage, as confirmed by the increased adsorption capacity of the materials. This is generally expected since the higher the amount of adsorbent in the aqueous reaction medium, the greater the number of adsorbate ions binding sites. The general

principle of surface chemistry of materials revealed that surface area increases by increasing the adsorbent dosage [59] and therefore, the observed increase in the number of Cr ions uptake by the materials is not unlikely. Accordingly, it was observed that high adsorption efficiency occurred, particularly in the transition change of the amount of adsorbent between 0.4 and 0.8 g and after which the adsorption sites of the chitosan-modified-activated carbon became saturated and the adsorption curves level off in response to full coverage of the active binding sites, which is independent of the adsorbate concentration [59]. This further confirms that after a certain dosage of the adsorbents, an equilibrium state was established— a point where the rate of adsorption balanced the rate of desorption. This means that the amount of Cr ions adsorbed by the chitosan-modified-activated carbon and the amount of unbound Cr ions in the liquid phase remained constant despite a further increase in adsorbent dosage. It is therefore evidently clear that 92 % removal of Cr ions was remarkably achieved with chitosan modified-activate within the range of adsorbent dosage used in the adsorption study. This was achieved with a dosage of 0.8 g and thus, was an optimum dosage for the effective removal of Cr ions over chitosan-modified-activated carbon.

On the other hand, the influence of adsorbent dose on the adsorption performance of unmodified activated carbon followed the same trend as the former material but varied significantly concerning adsorption capacity where the maximum amount of Cr ions adsorbed from the aqueous phase was 62 % with the optimum dosage of 0.8 g of unmodified activated carbon. The variation could be attributed to the free amino group (-NH_2), a hydroxyl group (-OH) and other surface functional groups on the chitosan. This is generally expected since disparity in adsorption capacities amongst different adsorbents depends on the difference and extent of surface modification [60, 61]. However, with an optimum dosage value of 0.8 g of chitosan-modified-activated carbon, the remarkable removal of Cr ions from an aqueous environment is assured under such conditions for the adsorption process.

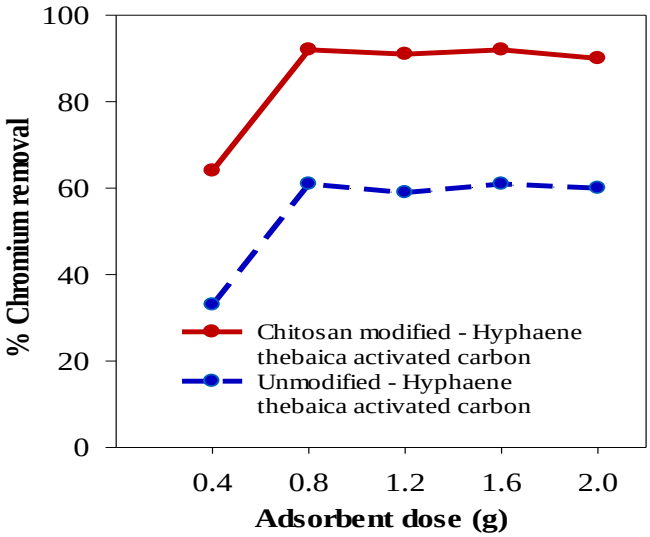

Figure 6. Effect of adsorbent dosage on chromium ions adsorption over chitosan modified and unmodified activated carbons of *Hyphaene thebaica*.

3.6 Effect of pH

The influence of pH on the chromium removal efficiency was investigated by varying the pH of the adsorption solution between 4 and 9. The choice of pH was guided by several studies conducted on the physicochemical characteristics of effluents of various industries with the majority of their pH values within the pH range of 4 to 9 [62, 63, 64]. The observed results for the effect of pH on chromium removal are presented in Fig. 7. Notably, the adsorption of Cr ions was strongly affected by the influence of the pH of the adsorption solution. It was observed that the Cr ions uptake by both chitosan-modified and unmodified activated carbons decreased with the increase of pH of the adsorption solution.

With the progressive increase in pH of the solution from 4 to 9, there was a consequential decrease in the adsorption of Cr ions from 96 to 77 % and 71 to 42 % over chitosan-modified activated carbon and unmodified activated carbon, respectively. This trend possibly occurred due to the fact that at high pH surfaces of adsorbent materials were mainly surrounded by hydroxyl groups (-OH), which presumably disfavoured the $Cr_2O_7^{2-}$ ions interactions with binding sites of both the adsorbent by enhanced repulsive forces and thus broke the adsorption potential of the adsorbents. However, under low pH conditions (acidic), the amino ($R\text{-}NH_3^+$) and the hydroxyl ($R\text{-}OH_2^+$) groups were protonated and the molecules of chitosan modified-activated carbon in the solution became sort of polycations and consequently increased the number of active sites available for the adsorption of Cr (VI) ions. On the contrary, on the surface of unmodified activated carbon, it was only the hydroxyl ($R\text{–}OH_2^+$) groups were presumably and primarily protonated. This is what distinguishes and accounts for the higher adsorption capacity of chitosan-modified activated carbon than an unmodified form of the material under the acidic pH condition. Therefore, this result indicates that the optimum operating pH condition required is 4 (acidic media), where the surface of chitosan-modified-activated carbon was more positive charges. This equally favours the adsorption of anionic Cr ions due to increased electrostatic attraction between the positively charged chitosan-modified activated carbon and negatively charged Cr (VI) ions.

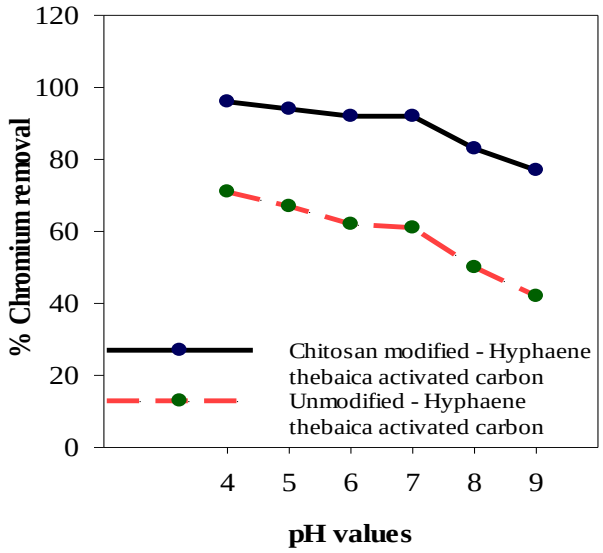

Figure 7. Effect of pH on the adsorption of chromium ions over chitosan-modified and unmodified activated carbons of *Hyphaene thebaica*.

3.7 Effect of other competing metal ions on the adsorption of chromium ions

Investigating the effect of competing metal ions of Cd, Ni, and Pb became necessary since their concentrations in the tannery wastewater exceeded the threshold limits of both WHO and USEPA guidelines and thus, cannot be tolerated as the concentrations can be offensive to the aquatic ecosystem. Besides, the activated carbon in chitosan-modified sorbents forms complexes with transition metal ions [65]. Therefore, the removal of chromium from the real tannery wastewater can be affected by the presence of Cd, Ni, and Pb due to their affinity with activated carbon— a part of chitosan-modified adsorbent. Accordingly, the real tannery wastewater was used to assess the suitability of the chitosan-modified-activated carbon adsorbent for practical use. In the assessment, the removal of Cr ions from the tannery wastewater was experimented with using chitosan modified-activated carbon of *Hyphaene thebaica* at the optimum conditions of pH 4.0, an adsorbent dosage of 0.8 g/100 ml, initial Cr, Cd, Ni, and Pb concentrations were 11.5, 0.92, 0.81, and 0.64 mg/L, respectively and contact time of 90 mins. The results of the adsorption study are shown in Table 3. Despite the competing divalent metal ions, 97.2 % removal of Cr (VI) ions was remarkably and efficiently achieved. However, the removal efficiency of Cd, Ni, and Pb were 89.1, 88.9 and 92.2 %, respectively. This indicates that

chromium has a higher affinity for chitosan-modified-activated carbon than the other metals. The results further suggest a low degree of competition between chromium and other competing metals, which perhaps resulted from the fact that divalent metal ions utilized more of the active adsorption sites on the activated carbon that has a high density of carbonyl, carboxylic, as well as hydroxyl that gave more binding groups and used to adsorb the divalent metal ions in the real tannery wastewater. In addition, under optimum conditions, the experimentally determined performance of chitosan-modified-activated carbon revealed that the material worked perfectly even at low residual chromium concentration in the tannery wastewater. This is important when the eventual purpose is to accumulate more sorbate at low residual sorbate concentrations, which is the case required mostly to meet regulatory agencies' limits. It means that the material exhibited superior performance even at low chromium concentration in the presence of competing metal ions in the tannery wastewater, particularly when the limitation of the maximum residual sorbate concentration is of environmental concern.

The outstanding performance of chitosan modified-activated carbon in the removal of Cr ions in the real tannery wastewater could be linked to a combination of many factors, namely the surface net charge of the adsorbent material and the nature of a charge on the metal ion itself under the optimum operating conditions [5]. In wastewater produced from the tanning process, chromium exists in two ionic forms, namely Cr (III) and Cr (VI) as cationic and anionic, respectively depending on many environmental conditions amongst which pH is of significant importance [66]. For example, in a well-aerated water environment, chromium occurs as anionic while in anaerobic conditions transforms into cationic species [25]. Accordingly, chromium and some other metal ionic species such as arsenic, depending on the pH of an aqueous environment, are known to exist in anionic forms. Amongst the chromium species, chromium (VI) forms a stable anionic species, namely $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and $HCrO_7^-$, depending on its concentration and pH [67].Therefore, pH is one of the major factors that control the overall behaviour of charged particles in an aqueous environment. In addition, pH has greatly influenced the adsorption process because of its effects on the surface charge and surface adsorption sites of adsorbents [67]. the pH of a solution also influences adsorption through modification of the surface functional groups of adsorbents [68]. However, activated carbonis adsorbent material with amphoteric characteristics depending on the pH of the solution and thus, their surfaces may be positively or negatively charged or even sometimes electrically neutral [10]. Hence, the adsorption of anionic species is favoured at lower pH while higher pH values favour the adsorption of cations [68, 69]. This justifies that Cr ions in the real tannery wastewater existed in either of the anionic forms of the metal such as CrO_7^{2-}, $HCrO_4^-$, and CrO_4^{2-} and $HCrO_7^-$since the optimum pH value used for the adsorption process was 4, which largely favours adsorption of anionic species of Cr because of its electrostatic interactions with the protonated amino ($R\text{-}NH_3^+$) and hydroxyl ($R\text{-}OH_2^+$) groups of the molecules of chitosan modified-activated carbon.

Table 3. Adsorption values were obtained for the removal of chromium ions by Chitosan-modified Hyphaene thebaica-activated carbon at optimum conditions.

Competing metals	C_e (mg/L)	q_e (mg/L)	q_t (mg/g)	% Removal
Cr	0.320	1.370	0.018	97.200
Cd	0.100	0.530	0.007	89.100
Ni	0.090	0.160	0.006	88.900
Pb	0.050	0.440	0.005	92.200

Optimum operating conditions; Cr = 11.5 mg/L, Cd = 0.92 mh/L; Ni = 0.81 mg/L; Pb = 0.64; pH = 4.0, and adsorbent dosage = 0.8 g/100 ml, contact time = 90min

For comparison, the removal efficiencies of some activated carbons and other adsorbents derived from various waste sources are provided in Table 4. The adsorbents were applied on various

adsorbates mostly for water purification, but only the case in which they had the best performance is reported. Considering the table, it is seen that the chitosan-modified activated carbon in the current work has higher removal efficiency (97.2%) than all the adsorbents reported here.

Table 4: Removal efficiency of some waste-derived adsorbents

Waste-derived Adsorbents	Removal efficiency	Reference
Wheat bran	90	70
Maa bamboo	91.7	71
Composite waste of peanut shell, coffee husk, corn cob & banana peel	96.2	72
Coconut shell	68.39	73
Banana peel	86.56	73
Orange peel	86.56	73
Chitosan modified polymer	80%	74
Wood waste	69%	75
Distillery sludge	82%	76
Citrus peel	58.97%	75

3.8 Adsorption isotherms

The adsorption equilibrium relationship between the solid phase (adsorbent materials) and liquid phase (adsorbates) is commonly established by isotherms. The equilibrium data for chromium ions adsorption by chitosan-modified and unmodified activated carbons are fitted both for Langmuir and Freundlich isotherm models, which are the most commonly used models for describing the process of adsorption as well as the nature and extent of distributions of adsorbates over the surface of adsorbents. The isotherm constant parameters and regression coefficient (R^2) which use to judge the fitness of the models for an adsorption process are presented in Table 5 as well as in Fig. 8 and 9. From the Table, the correlation coefficients obtained for validation of the fitness of the Langmuir model for adsorption of chromium ions over chitosan modified-activated carbon and unmodified activated carbon are 0.1690 and 0.8828, respectively. As the value for unmodified adsorbent is greater than 0.5 and close to 1, it is confirmed that the mechanistic behaviour of the adsorption processes over the prepared adsorbents fit the Langmuir isotherm model. However, the low R^2 value obtained for the chitosan-modified adsorbent suggests that the model is quite unsuitable to explain the adsorption process of chromium ions over both the chitosan-modified and unmodified adsorbents since the model constants are a symbolic measurement of surface binding energy that describes affinity for adsorbate by adsorbent and monolayer coverage [77, 78]. It is therefore inferred that the surface and the pores of both chitosan-modified and unmodified activated carbon synthesized from *Hyphaene thebaica* shell are heterogeneous and played a vital role in chromium adsorption. On the separation factor, R_L, its values are also negative, which suggests that the adsorption of the chromium on the chitosan-modified and unmodified activated carbons was difficult [79].

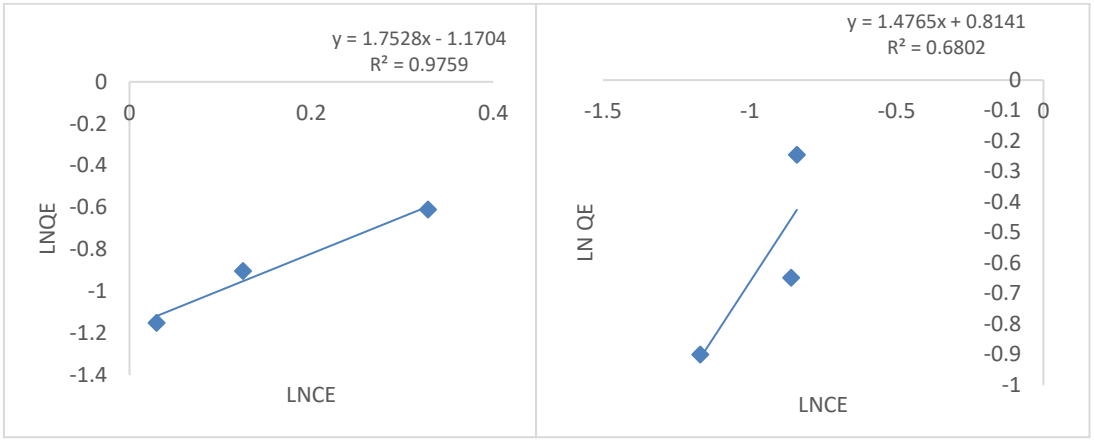

Figure 8. Freundlich Isotherm Plot for adsorption of Chromium by (a) Activated carbon of Hyphaene thebaica and (b) Activated carbon of Chitosan modified Hyphaene thebaica.

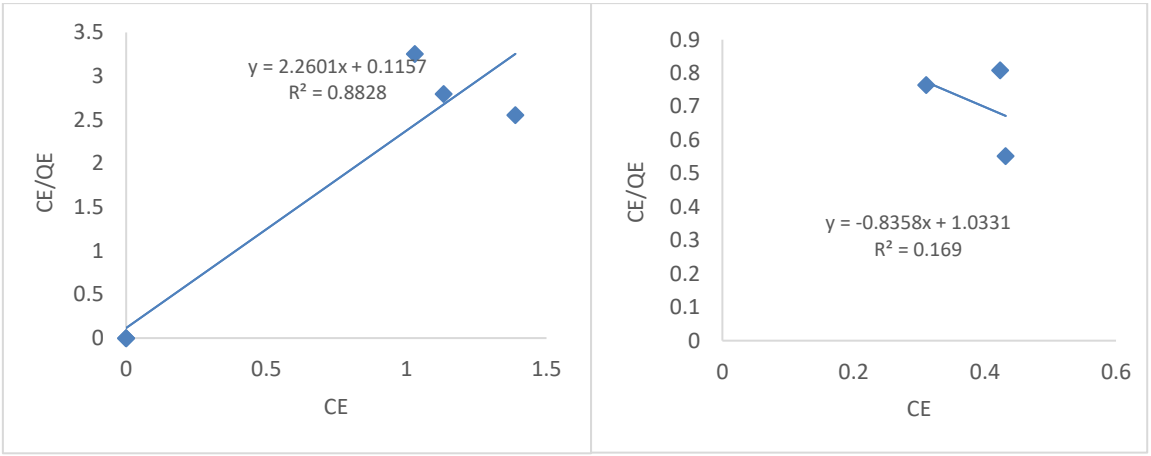

Figure 9. Langmuir Isotherm Plot for adsorption of Chromium by (a) Activated carbon of Hyphaene thebaica and (b) Activated carbon of Chitosan modified Hyphaene thebaica.

However, the chromium ions adsorption process is well fitted to the Freundlich isotherm model, as adjudged by strong correlation coefficients, R^2 values that are very much close to one (1) and much greater than the correlation coefficients obtained for the Langmuir model (Table 5). Unlike the Langmuir isotherm model, which is based on equal affinity binding sites, formation of monolayer and absence of lateral interaction between adsorbates amongst others, the Freundlich isotherm takes the heterogeneity of adsorption and roughness of adsorbent surface into cognizance. In the linear transformed Freundlich equation, 1/n defines the surface heterogeneity of an adsorbent, the smaller its value, the greater the extent of heterogeneity of an adsorbent surface. Therefore, if the n value is between 1 and 10, the adsorption is a favourable process [80]. As such, the adsorption process of chromium by both the two adsorbents fits well and is best described by the Freundlich isotherm model, as the experimental data obtained for Freundlich constants, K_F and n, are found to be 2.2571 and 0.677 as well as 0.310 and 0.571 for chitosan modified-activated carbon and unmodified activated carbon, respectively. This is further supported by an excellent correlation coefficient, R^2 values very near unity (Table 5). Accordingly, the Freundlich isotherm model is favoured and therefore, this accounts for the heterogeneous nature of the surfaces of the adsorbents with mixed regions of binding sites occurred with the —C=O, —COO^-, –OH and –OH_2^+, R–NH_2 and R–NH_3^+ groups, particularly in the chitosan modified-activated carbon, although depending on the pH of the adsorption solution.

Table 5. The Langmuir and Freundlich model constant parameters and their corresponding regression coefficients (R^2)

Adsorbents	Metal	Langmuir Parameters				Freundlich Parameters		
		q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (L/mg)	R^2
Chitosan modified-activated carbon	Cr	1.196		0.09705	0.169	0.677	2.257	0.996
Unmodified activated carbon	Cr	0.442	19.64	0.00442	0.883	0.571	0.310	0.976

3.9 Adsorption kinetics

The experimental kinetics of chromium adsorption data was tested in terms of pseudo-first order, pseudo-second order, and intra-particle diffusion. However, by far it is pseudo-second-order kinetic model that was successfully applied to the adsorption process of chromium over the chitosan-modified and unmodified activated carbons. Primarily, the description of pseudo-second order is based on the postulation that the rate-determining step is chemisorption, which emphasises electrons exchange between adsorbent and adsorbate [81, 82].

The adsorption data derived from the application of the pseudo-second order kinetics model are shown in Table 6 and Fig. 10. The data favoured the kinetic model, which is supported by a strong correlation coefficient value (R^2=0.99). The adsorption mechanism is well explained in terms of cationic and anionic exchanges over the surfaces of the materials, as inferred earlier. Because mixed regions of binding sites that occurred with the ─C=O, ─COO^-, –OH and –OH_2^+, R–NH_2 and R–NH_3^+ groups, particularly in the chitosan modified-activated carbon, by implication, confirms the predominance of surface chemisorption. Consequently, the pseudo-second-order kinetics model ruled out the influence of the pseudo-first-order and diffusion kinetics, which are more inclined towards physisorption with the assumption that sorbate binds only to sole adsorption sites on the adsorbent surface without participatory chemical reaction between adsorbate and adsorbent [83,84,85]. This further suggests that the adsorption mechanism for chromium over the two prepared adsorbent materials was chiefly chemical adsorption. However, the k_2 value for the adsorption of chromium ions over chitosan modified-activated carbon is higher (0.0544g/mg min) than adsorption over unmodified activated carbon (0.3615g/mg min) and therefore, indicates that chromium adsorption by former material was faster. This may be attributed to the additional amino surface functional group (–NH_2) that served in the materials as a nucleophile for the protonation process and subsequently created affinity sites for negatively charged atomic nuclei of $Cr_2O_7^{2-}$, which was augmented by the chitosan matrix [86].

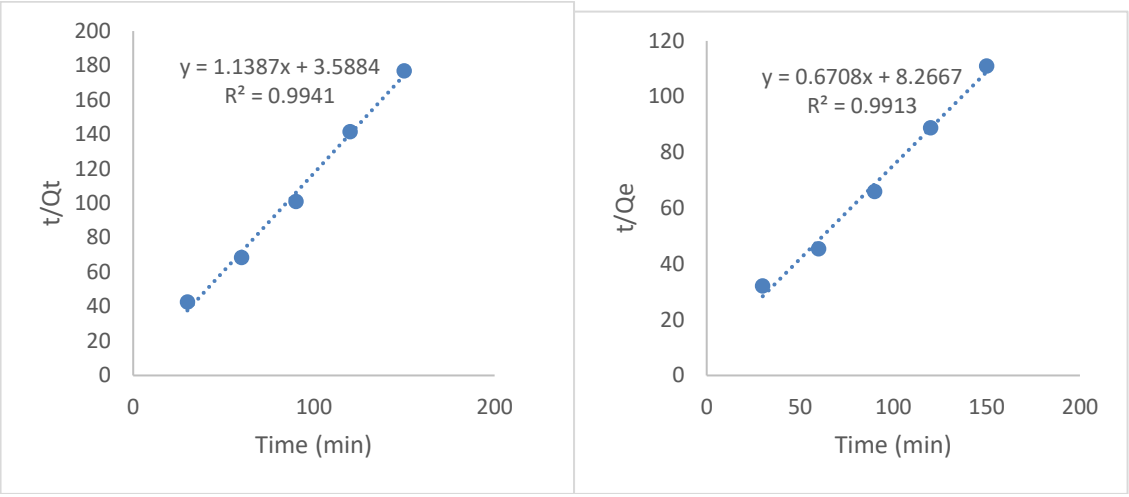

Figure 10. Kinetic Plot for adsorption of Chromium by (a) Activated carbon of *Hyphaene thebaica* and (b) Activated carbon of Chitosan modified *Hyphaene thebaica*.

Table 6. Pseudo-second order kinetics model constant and its corresponding regression coefficient (R^2)

Adsorbents	Metal	Pseudo-second order kinetics		
		q_e(mg/g)	k_2 (g/mg min)	R^2
Chitosan-modified activated carbon	Cr	1.491	0.0544	0.991
Unmodified activated carbon	Cr	0.878	0.3615	0.994

Conclusion

In this study, activated carbon was successfully derived from the shells of *Hyphaene thebaica* and modified with commercially based chitosan through impregnation. The resultant surface modification of the derived activated carbon produced a microporous adsorbent material with excellent surface properties that influenced high adsorption capacity. The adsorption parameters were optimized through batch experiments. The optimum contact time and the optimum adsorbent dosage were 90 min and 0.8g/100mL respectively while the optimum pH was 4. The equilibrium data were evaluated using Freundlich and Langmuir isotherm models. The Freundlich model showed a better fit indicating the favourability of multilayer adsorbate formation on the heterogeneous surface of both chitosan modified and unmodified *Hyphaene thebaica* activated carbon. The equilibrium data were also tested with different kinetic models. However, the kinetic data showed a better fit with the pseudo-second order kinetic model with a correlation coefficient (R^2) value of 0.9941. On a comparative basis, the Chitosan-modified *Hyphaene thebaica* performed better with Cr ions removal efficiency of 97.2% than the unmodified *Hyphaene thebaica* with a maximum uptake capacity of 62%

Hence, the chitosan-modified-activated carbon has shown to be useful in the removal of chromium ions from tannery wastewater. However, in future research work, it is important to investigate whether other anionic ions present in tannery wastewater could interfere with the adsorption process of $Cr_2O_7^{2-}$ ions.

Authors' declaration

All the authors of this research paper have declared that this research work or a part of it has not been previously published anywhere and is not under consideration in other peer-reviewed journals in the same form. The authors have unanimously agreed and approved the research article to be published as submitted to the journal.

Conflicting interests

This is to declare that all the authors do not have any financial conflicting interests or personal relationships that undermined and could have influenced decisions on the entire work reported in this paper.

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