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Chromium Adsorption Using Modified Locust Bean and Maize Husk

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ABSTRACT

Carbon-based adsorbent from the hardwood of locust bean and maize husks were assessed for their potential in reducing Cr^{6+} ions in contaminated industrial effluent waters. Two samples of activated carbon (AC) were successfully prepared by a simultaneous two step carbonization and activation processes using maize husk (*Zea mays*) and locust bean (*Entada africana*). Chemical activation was achieved by first impregnating the prepared raw materials with 60 % (v/v) and 80 % (v/v) H_3PO_4 acid and thereafter subjected to carbonization at 550°C and 950°C for a period of 1½ hr and 4 hr, respectively. The ACs were characterized and isotherm plot was produced for the adsorption of methylene blue (MB) from which the adsorption capacity was calculated. The effect of pH, adsorbent dosage and time were studied. The results showed large surface area (115.69 to 143.74 m^2/g), as suggested by the SEM result, which indicates the possibility of high adsorption of Cr^{6+} at pH 2 – 6, and that was due largely to HCrO_4^- than by any other Cr^{6+} species. The pseudo-first order kinetic best described the data obtained and so suggest physisorption mechanism involved in the adsorption of Cr^{6+} unto LBAC and MHAC. The relatively high percentage ion removal by LBAC and MHAC suggests that they can be used as inexpensive, efficient and environmentally friendly alternatives in the cost-effective removal of Cr^{6+} from industrial wastewaters when these modification conditions are used.

Keywords: Activated carbon, Adsorption, Chromium, Locust bean, Maize husk

INTRODUCTION

Heavy metal pollution is a serious problem today and its removal from the environment is of serious concern due to their bioaccumulation and persistence in the environment [1]. Like organic pollutants, most heavy metals do not undergo biological degradation into harmless end products [2]. Chromium's applications are in chrome plating, stainless steel and in metal ceramics alloys. Chromium plating was once widely used to give a polished mirror finish steel [3]. In metallurgy, Cr is used to give a shiny finish, corrosion resistance and to harden stainless steel [4]. It is also used as industrial catalyst and pigments in dyeing and tanning of leather. Cr (IV) oxide (CrO_2) is used in the production of magnetic tape [5].

People could be exposed to Cr via inhalation, ingestion and through dermal contact with Cr or Cr compounds since Cr is produced in environmental matrices such as air, water and soil [6]. The level of Cr in air and water is generally low. In drinking water, the level of Cr is low as well, but Cr contaminated well water may contain the dangerous Cr (IV) [7]. For most people eating food that contains Cr (III) is the main form of Cr uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains [7]. Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes [8], but the uptake of too much chromium (III) causes skin rashes. Cr (VI) is dangerous to health especially for those that work in chromium-plating and textile industries. Tobacco smokers also have a higher risk of exposure to chromium effects [9]. Cr can cause nose irritations and nose bleeds after breathing in Cr (IV). Other health problems that are associated

with chromium (VI) are: stomachs ulcers and upset, respiratory complications, genetic material alteration, lowering of the immune system, liver and kidney problems and even death [10].

The oxidation state of Cr determines the health hazards associated with its exposure. Chromium metal ions cause diseases such as liver damage, nephritis and stomach distresses. Cr (VI) ions are the major cause of nasal mucous ulcer [11].

Industrial applications of adsorbents became a common practice following the widespread use of charcoal for decolorizing liquids and, in particular, its use in gas mask during the 1914-1918 World War for the protection of military personnel from poisonous gases [12]. Adsorbents for the drying of gases included alumina, bauxite, and silica gel; bone char and other carbons were used for sugar refining and the refining of some oils, fats and waxes. Activated charcoal was employed in the recovery of solvents, elimination of odours and the purification of air and industrial gases. Fuller's earth and magnesia were found to be active in adsorbing contaminants of petroleum fractions and oils, fats and waxes [13]. Base-exchanging silicates were used for water treatment while some chars were capable of recovering precious metals [14]. A major limitation to the use of non-carbon-based sorbents in water purification is that they are expensive. Hence, there is a need for the development of safe and low-cost alternatives to the expensive and commercially available adsorbents. Many researchers have successfully investigated the production of carbon-based adsorbents using agricultural wastes [15] such as sugarcane bagasse [16], African canarium seed [17], Oil bean and snail shell [18], rice husk [19], sawdust, coconut husk [20], oil palm shell [21], for the removal of heavy metals from wastewater. According to Choudhari [15], a low-cost adsorbent requires less processing, abundant in nature and could be waste material and by-products and, higher adsorption capacity may offset the cost of additional processing if required. Ajayi-Banji [22], modified Locust bean to char and used it in heavy metal sequestration but not chromium. Jalil *et al*, [23], chemically (Ca (OH)₂) modified and calcined maize husk and used it to adsorb malachite green, but Indah *et al*, [24] did not modify it and used it to remove iron from aqueous solution. Therefore, this study seeks to explore Locust bean and Maize husk, as heavy metal (chromium) adsorbents from aqueous solution at these different modification conditions.

EXPERIMENTAL

Standard stock solutions

Standard Stock Solution of K₂Cr₂O₇ (1000 mg/L); Activating Chemical, H₃PO₄ (Concentrations of 40%, 60% and 80%); 1,5-Diphenylcarbohydrazide solution (DPC) (1%); Methylene Blue stock (1000 mgL⁻¹) Solution Blank solution for control. All reagents were purchased from Sigma-Aldrich Company.

Adsorbent

The activated carbons used in this study were produced from the hard wood of a locust bean and from maize husks. The raw materials were first cut into small sizes before washing thoroughly with water and allowed to dry in an oven at 105^oC. After cooling to room temperature, they were soaked in 80% and 60% phosphoric acid (H₃PO₄), respectively. Each mixture was allowed to impregnate for 48 hours after which the acid was drained off and the base materials dried to constant weight at 105^oC. The locust bean and maize husks impregnated materials were simultaneously carbonized and activated in a muffle furnace at the optimized conditions of 900^oC for 4 hours and 550^oC for 90 minutes, respectively. When the activation time was reached, the furnace was disconnected from the power supply and the carbon allowed to cool in the absence of air. The cooled carbon was pulverized further, filtered with 125 - 45 μ m sieve and then washed with de-ionized water till a near neutral pH (6.3) was achieved on the carbon surfaces. In the designation of the carbons, LBAC refers to locust bean based activated carbon and MHAC represents activated carbon from maize husks.

Characterization of Activated Carbons (AC)

Ash content determination

The percentage ash content was determined according to the ASTM D2866-94 method. Dry AC sample (1.0 g) was placed in ceramic crucible and moved into a heated muffle furnace at 1000 ^oC. The furnace was left on for one hour after which the crucible and its content was transferred to desiccator and allowed to cool. The crucible and content were reweighed and the weight lost was recorded as the ash content of the AC sample (W). Thereafter, percentage ash content (dry basis) was calculated using equation 1.

$$\% \text{ Ash} = \frac{w_3 - w_1}{w_2 - w_1} \times 100 \quad (1)$$

where, W₁ = Weight of the crucible (g); W₂ = Weight of the crucible + Activated carbon sample (g); W₃ = Weight of the crucible + ash containing sample (g).

Moisture content determination

Approximately 1.0 g of powdered AC was weighed into a crucible. The crucible was positioned in a hot electric oven maintained at about 110 ^oC. The sample was constantly removed and reweighed at a 30 min interval until a constant weight (W) was obtained. The crucible and its content was retrieved and cooled in desiccator. The percentage moisture content was calculated using equation 2.

$$\% \text{ Moisture} = \frac{w_2 - w_4}{w_2 - w_1} \times 100 \quad (2)$$

where, W₁ = Weight of the crucible (g); W₂ = Weight of the crucible + Activated carbon sample (g); W₄ = Weight of the crucible + ash containing sample (g).

Specific surface area by methylene blue (MB) equilibrium adsorption

The experimental standard MB solution was prepared by diluting the stock solution with de-ionized water to obtain concentrations of 10, 20, 30, 40 and 50 mg/L. The initial absorbance of MB was determined at 630 nm by the UV – visible spectrophotometer [25]. The Methylene blue number was determined according to the Method of Joshi[26]. In this test, 0.02 g of each prepared activated carbon was mixed with 25 cm³ of methylene blue (MB) solution in several conical flasks separately at the different concentrations (10 - 50 mg/L). After shaking for 4 hr, the mixture was allowed to stand for additional 20 hr. The suspensions were filtered and the amount of MB remaining in the solution was determined through absorbance measurement.

C₁ and C₂ represent concentrations of MB in solution before and after its adsorbance by individual AC and A₁ and A₂ represent their spectrometric absorbance respectively. Then, At equilibrium, A₂/A₁ = C₂/C₁ giving C₂ = (A₂/A₁) *C₁. The surface area was calculated from equation 3 [25].

$$S_{MB} = \frac{6.022 \times 10^{23} \times a_{MB} \times q_{max}}{100 \times M_{MB}} \quad (3)$$

where S_{MB} is the specific surface area, q_{max} is the amount of methylene blue adsorbed at the monolayer of adsorbent, a_{MB} is the occupied surface area of one molecule of methylene blue (197.2 Å²)

Surface morphology and functional group

SEM was used to study the surface morphology of the adsorbents produced. The micrograph was taken at the Department of Chemical Engineering, Ahmadu Bello University, Zaria. Also, FTIR (JASCO FTIR-3500) was used to identify the functional groups present on the surface of the modified LBAC and MHAC.

Equilibrium adsorption

Eight (8) portions of 50 cm³ Cr⁶⁺ stock solutions with an initial concentration of 50 mg/L were treated with 0.5 g of the activated carbon. Prior to the addition of the adsorbent, the initial pH of the solutions was adjusted by drop-wise addition of 0.1 M HCl and/or 0.1M NaOH solution. The batch test was carried out for a pH range of 2.0 – 8.0. The study was conducted by introducing 0.5 g of the adsorbent into 50 cm³ of the metal ion solutions contained in beakers. The beakers were placed on an orbital stirrer and the speed set to 125 rpm. Components of the mixtures were allowed to contact and equilibrate for 2hr after which each mixture was filtered. 5 drops of DPC solution were added to every 30 cm³ portion of the filtrates containing Cr⁶⁺ ions after acidification with 1.0 cm³ of H₃PO₄ solution. The solutions were kept for few seconds (during which a red-purple coloration developed) and then analyzed for the equilibrium concentration of Cr⁶⁺ in the solution, using UV- Spectrophotometer. Due to the doubtful high values of % adsorption of Cr⁶⁺ at very low pH, all the other batch experiments were conducted at pH = 4 for Cr⁶⁺.

The effect of adsorbent dosage

Weighed quantities, in the range of 0.1 – 1.1 g, of each carbon were brought into contact with 50 cm³ portions of several 50 mg/L solutions of Cr⁶⁺ for a space of 2hr. The adsorption study was performed at a fixed pH = 4.

The study the effect of contact time on the adsorption of Cr⁶⁺

0.5 g of activated carbon was placed in 6 separate conical flasks containing 50 cm³ of 50 mg/L of Cr⁶⁺ ions. The mixtures were mixed very well in a shaker and kept to equilibrate under room temperature condition. Each of the flasks was removed and content analyzed at intervals of 20, 40, 60, 80, 100, and 120 min. Filtrates were treated as usual to determine the amount of Cr⁶⁺ species left after adsorption.

The pattern of adsorption of these ions on the adsorbents was modeled by adding 50 cm³ of 20, 40, 60, 80, and 100 mg/L solutions of each ion into glass beakers. A fixed amount of 0.5 g of the carbon was introduced. After treatment as in earlier experiments, the mixtures were then separated by filtration.

The final concentrations of ions at equilibrium were measured using the absorption instruments. The amounts of ion adsorbed at equilibrium, q_e (mg/g) were calculated from (1).

$$\text{Equilibrium adsorption, } q_e = \frac{C_i - C_t}{S} \quad (1)$$

Where, q_e is the quantity of ion adsorbed at time, t (mg/g). C_i and C_t (mg/L) is the liquid phase concentration at initial and any time t, respectively, S is the dosage. The adsorption kinetics were investigated using data obtained from “Batch studies on effect of contact time, at 50 mg/L. A number of adsorption kinetics models have been established to understand the adsorption kinetics and rate limiting step. The pseudo-first order model [27] was used for the adsorption of liquid adsorbate on solid adsorbent on the basis of adsorption capacity at different time intervals.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively. k₁ is the pseudo-first order rate constant of adsorption (min⁻¹). After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t to (2), we get a linear form as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

log(q_e - q_t) was plotted against t, and the values of the constants q_e & k₁ were calculated. The pseudo-second order model is based on certain assumption that the adsorption of adsorbate onto adsorbent supports second order chemisorptions.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 is the pseudo-second order rate constant of adsorption (g/mg/min).

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of (4) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (5)$$

(5) is the integrated rate law for pseudo-second order chemisorption reaction, and can be rearranged to obtain

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

By plotting a curve of t/q_t versus t , values of q_e and the pseudo-second order rate constant of adsorption, k_2 (g/mg/min) were evaluated. The nature of adsorption (i.e monolayer or multilayer adsorption) of these ions on the adsorbents was investigated by adding 50 cm³ of 20, 40, 60, 80, and 100 mg/L solutions of each ion into glass beakers. A fixed amount of 0.5 g of the carbon was introduced. After treatment as in earlier experiments, the mixtures were then separated by filtration. The final concentrations of ions at equilibrium were measured using the absorption instruments. The amounts of ion adsorbed at equilibrium, q_e (mg/g) were calculated from equation 1.

RESULTS AND DISCUSSION

Table 1 presents the moisture, ash, methylene blue and surface area of the activated carbon. Ash content is less important except where the carbon is used as a catalyst support since certain constituents of the ash may interfere or destroy the action of precious metal catalysts. Ash content also influences the ignition point of the carbon; this may be a major consideration where adsorption of certain solvents is concerned [28]. High ash content is undesirable for AC since it reduces the mechanical strength of the AC and affects the adsorptive capacity as well [29]. Abdullah *et al*, [30], opined that ash content of 1 to 20% make a carbon suitable adsorbent, thus making LBAC and MHAC a good adsorbent with respect to their ash values. Moisture content according to Aziza [31], has a relationship with porosity of AC. Adsorbents with high moisture content is expected to swell less, and so retard pore size expansion for adsorbate uptake [32]. It was observed that the moisture content fell within 14-23.51% indicating low moisture content of the carbon. The moisture content obtained is comparable with reported results (19.50 ± 0.020 by Ekpete and Horsfall, [33] 15.30 ± 1.15 by Ekpete *et al* [28]).

The observed large surface area 115.69 to 143.74 m²/g shows the possibility of high adsorption of Cr⁶⁺ and other pollutants from industrial waste. The surface area is an important attribute for consideration in the application of activated carbon [34].

Table 1: Moisture, Ash Content and surface area of the activated carbons (n = 3)

Parameter	LBAC	MHAC
% Moisture	23.51±8.30	14.00±2.87
% Ash	5.9±0.23	7.18±0.99
Methylene No, qm (mg/g)	45.25±3.70	35.21±1.34
Surface area (m ² /g)	143.74±1.11	115.69±2.21

The degree to which chemical species are dissociated and the forms in which they are found in aqueous media are functions of their solution pH. This singular factor determines the degree to which different forms of species are available, their mobility and most importantly, their ionic diameter. All the above factors put together exert a tremendous effect on the extent to which ionic species are removed from aqueous solutions by adsorption. The acidity/alkalinity of a solution determines the rate at which a metal will dissolve in it and hence, their concentration. Thus, pH is an important parameter to consider, especially in the advancement of adsorption technology.

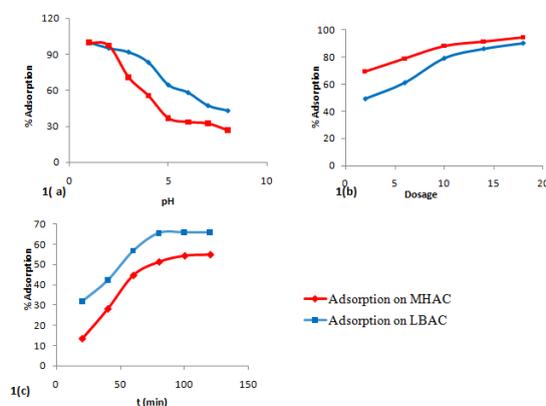


Figure 1: The effects of pH on adsorption of Cr (2a), effects of carbon dosage on adsorption (2b) and effects of contact time on adsorption (2c).

The effect of pH on adsorption of Cr⁶⁺ (Figure. 1a), shows that the highest % adsorption occurred between pH = 1 - 3 and thereafter decreased and this could be from the reduction of Cr⁶⁺ to Cr³⁺, a reaction that can occur only in acidic media or in the presence of reducing agents like Fe²⁺ ions.

The observation in this pH interval is quite negative as far as the research is concerned, however it could have been an enhancement if the redox product was substantially adsorbed. In solution, most Cr^{6+} species are anionic and it therefore becomes pertinent to explain the effect of pH on adsorption of Cr^{6+} on the basis of electrostatic or coulombic interactions between the carbon surfaces and the Cr^{6+} species present in the aqueous solution. At low pH values (acidic solutions, pH 2 – 5.5), the surface of the adsorbent becomes highly protonated, favouring the uptake of Cr^{6+} in the anionic forms. With an increase in pH, the degree of protonation of carbon surfaces reduces gradually and hence, adsorption decreases. The speciation diagram shows that the predominant Cr^{6+} species in aqueous solution are HCrO_4^- (bichromate) and CrO_4^{2-} (chromate) anions in the pH range of 2 – 12 [35]. According to Rivera-Utrilla HCrO_4^- exists in larger amount than any other Cr^{6+} species at pH = 2 – 4 whereas CrO_4^{2-} is more stable and predominates at pH > 7. Rivera-Utrilla [36], further observed that the molar percentage distribution of HCrO_4^- and CrO_4^{2-} were respectively given to be 95% & 5% at pH = 5, 80% & 20% at pH = 6, and 2% & 98% at pH = 8. This means that within the pH of our study (2 – 8), the Cr^{6+} was adsorbed on the carbon as either the HCrO_4^- or CrO_4^{2-} species. It has also been observed that, in acidic environments, Cr(VI) will be reduced to Cr(III) in an adsorbent. $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$; ($\text{Cr}_2\text{O}_7^{2-}$ under acidic conditions get reduced to Cr^{3+}), $\text{Cr}_2\text{O}_7^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$; (in basic solutions it is much less oxidizing and exists as $\text{Cr}(\text{OH})_3$ [37] (Mohanty *et al.*, 2006). Although CrO_4^{2-} ions are very much available and should have contributed more to improve % adsorption at pH > 6, there was rather but a decrease. This behaviour can be attributed to the dual competition of both CrO_4^{2-} and OH^- ions to be adsorbed on the active sites of the adsorbent of which OH^- predominates. Nassima and Moyssa, [38] equally noted that HCrO_4^- exists predominantly in solution over $\text{Cr}_2\text{O}_7^{2-}$ at pH = 2 – 6 and that is because the ionic size of HCrO_4^- is smaller than that of $\text{Cr}_2\text{O}_7^{2-}$, the HCrO_4^- has a greater possibility of being diffused and adsorbed easily onto the adsorbent surfaces compared to $\text{Cr}_2\text{O}_7^{2-}$. Therefore, we can conclude that the high % adsorption at pH = 2 – 6 was due mostly to HCrO_4^- than by any other Cr^{6+} species. This is in line with the observation of Mohanty. The better effect observed around acidic pH could be likened to the neutralization of negative charges on the surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of the hydrogen chromate ion (HCrO_4^-) and its subsequent adsorption. Because HCrO_4^- is the dominant anionic form of Cr(VI) between pH 2 – 6, this ionic form was found to be favorably adsorbed on the surface of LBAC or MHAC. The negative charges could result from oxygenated functional groups of basic attributes such as hydroxyl groups, chemisorbed at the surface of the pores [39].

The rate of adsorption of Cr^{6+} ion onto LBAC and MHAC was investigated as represented in Figure 1c which showed that adsorption was rapid within the first few minutes and thereafter increased slightly and slowly, attaining their maximum values at equilibrium. The observed trend of adsorption can best be explained in the premise that at zero time, there were large numbers of vacant active sites available for adsorption. However, with passage of time, the surface sites became gradually occupied and get exhausted at equilibrium [40]. Maximum adsorption was attained 100 min for Cr^{6+} on both LBAC and MHAC. By inference, LBAC have a stronger capacity for adsorption of the ions than MHAC.

Effect of dosage on percentage adsorption of metal ions onto activated carbon was studied under equilibrium conditions of pH = 4, contact time of 100 min and environmental temperature of 29 ± 0.5 °C. There were increases in adsorption as the adsorbent dosage increased (Fig.1b), and this could be as a result of increase in adsorbent surface area and availability of the more active sites. Adsorption increased almost linearly in a few minutes and thereafter progressed slowly which, if additional dosage had been used further, the % adsorption would have decreased to a constant value. According to Mohamed [41] (2012), the expected decrease in % adsorption with additional dosage would have been the effect of overlapping of adsorption sites as a result of overcrowding of adsorbent particles.

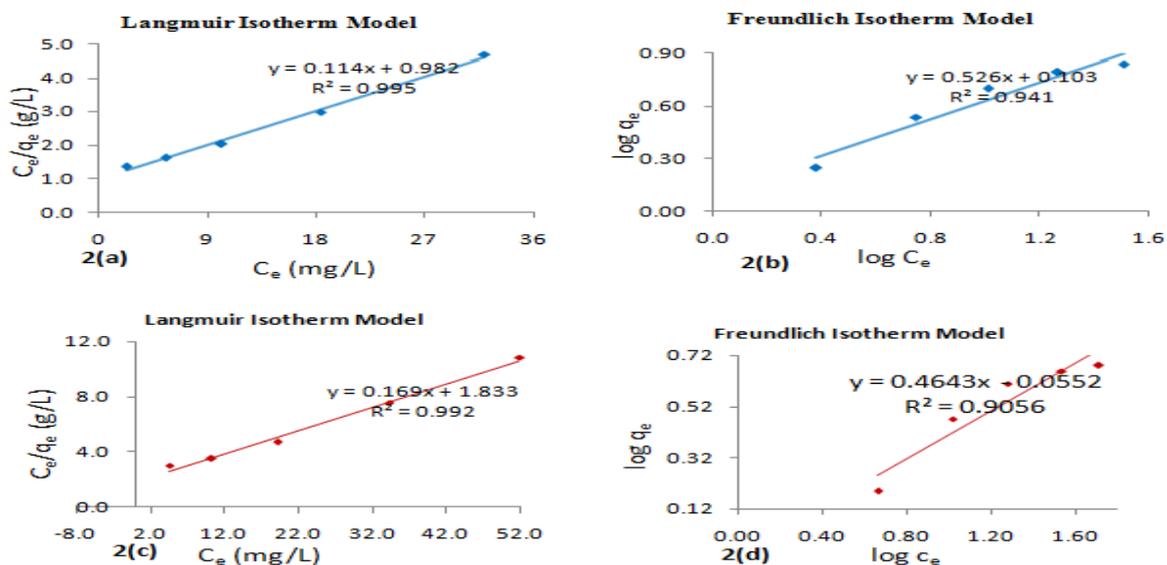


Figure 2: Langmuir isotherm for LBAC (2a), MHAC (2c) and Freundlich isotherm for LBAC (2b), MHAC (2d)

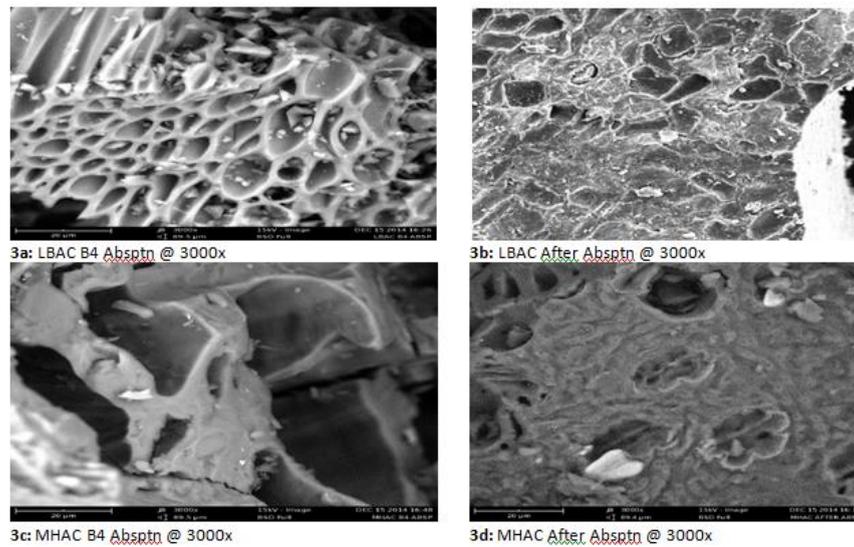


Figure 3: SEM Micrograph at 3000 magnification

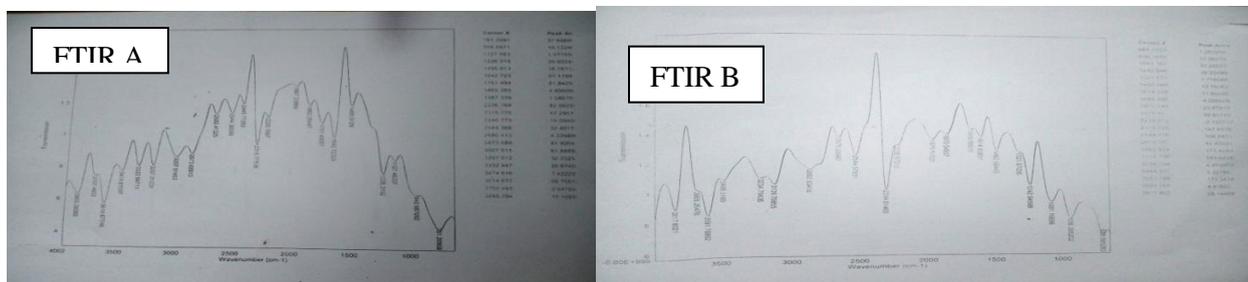


Figure 4: FTIR spectra of LBAC (A) and MHAC (B)

The surface morphology of the activated LBAC and MHAC is different from the used LBAC and MHAC (Figure 3) indicating the effect of adsorption onto the AC. The unused AC showed a rough surface area unlike the used AC which had a smooth surface indicating that the pores on the surface of the adsorbent have been occupied. The image of the AC before usage showed the outer surface is rough and discontinuous formation which can be considered as pores. It was observed from the SEM result, that the pores of the activated carbon were reduced or occupied as a result of adsorption of Cr⁶⁺ ions onto the surface of the adsorbents

The FTIR spectra (figure 4) showed the presence of carboxyl, hydroxyl, amine, amide, alkyl, aromatic C = C, nitrile, phenol and carboxylic functional groups on the surface of the activated carbon. The peak at 3000 – 2500 cm⁻¹ indicates the presence of O – H Str. of COOH, phenols and OH, and that between 2950 – 2850 cm⁻¹ showed the presence of C – H Str. of Alkanes and C = C Str. of Nitriles (Figure 4B). 2544.37 cm⁻¹ (Carboxylic Acid C –H Stretch) and 3207.012 - 3474.62 cm⁻¹ (Amine N-H Stretch) were also indicated in LBAC (Figure 4A). There was strong surface oxide re-organization as a result of the interactions of the atoms of the activating agents and heteroatoms present on the surface of the activated carbon [42]. Oxygen-containing surface functional groups are known to affect the adsorptive properties of activated carbons. Magne & Walker [43] 1986), found that acidic oxygen surface complexes decrease the chemisorption of phenols. The FTIR peak observed at 1210–1100 cm⁻¹ showed C-O stretching of alcohols which exhibited a relatively high IR intensity in LBAC compared to MHAC even though both were pre-treated with phosphoric acid. This promoted the formation of oxygen-containing functional groups which are closely associated with the adsorption of Cr [44]

Table 3: Kinetic Parameters for Cr⁶⁺ Adsorption onto Activated Carbon

AC	Pseudo-First Order Kinetic			Pseudo-Second Oder Kinetic		
	K ₁	q _e	R ²	K ₂	q _e	R ²
LBAC	6.35×10 ⁻²	176.7665	0.6831	4.73×10 ⁻⁴	54.054	0.9838
MHAC	5.27×10 ⁻²	88.4708	0.9481	8.79×10 ⁻⁵	70.4225	0.6966

Table 4: Langmuir Isotherm Constants

AC	qe (mg/g)	b/K _L = (L/mg)	R ²
LBAC	8.7719	0.1161	0.9952
MHAC	5.9067	0.0923	0.992
Freundlich Isotherm Constants			
AC	K _F [(mgg ⁻¹) (mg ⁻¹) ^{1/n}]	n	R ²
LBAC	1.2691	1.8993	0.9415
MHAC	0.8806	2.1538	0.9056

CONCLUSION

Characterization of the ACs showed LBAC had the best surface area, 143.74 m²/g and with the best-defined pores than MHAC. The presence of the oxygen-containing functional groups enhanced the adsorption process on the surface of the LBAC and MHAC. The adsorption isotherms investigation showed that the Langmuir adsorption isotherm is superior to Freundlich adsorption isotherm with higher coefficients of determination (R²) values, although, both isotherm models had comparably high fit for adsorption suggesting a possibility of the adsorption process obeying both models. The magnitude of the Langmuir constant, q_e indicates that the amount of Cr⁶⁺ per unit weight of LBAC (8.7719 mg/g) required to form a complete monolayer on the surface is significantly higher than its value of 5.9067 mg/g on MHAC. Langmuir constant b, was relatively low overall, confirming high affinity between the adsorbents and adsorbates. Within the pH of our study (2 – 8), the Cr⁶⁺ was adsorbed on the carbon as either the HCrO₄⁻ or CrO₄²⁻ species. Although CrO₄²⁻ ions are very much available and should have contributed more to improve % adsorption at pH > 6, there was rather but a decrease, caused by the dual competition of both CrO₄²⁻ and OH⁻ ions to be adsorbed on the active sites of the adsorbent of which OH⁻ was dominant. The pseudo-first order kinetic best fit the data and so suggest a physisorption mechanism in the adsorption of Cr⁶⁺ unto LBAC and MHAC. The relatively high percentage ion removal by LBAC and MHAC suggests that they can be used as inexpensive, efficient and environmentally friendly alternatives in the cost effective removal of Cr⁶⁺ from aqueous solution, though LBAC is a better adsorbent.

REFERENCES

- [1] L. Aljerf and M. Aljurf. Nutrition & Dietetics. **2020**.
- [2] U. Isah and M. Lawal, Advances In Applied Science Research. **2012**. 3(6): p. 4033-4035.
- [3] T. E. Graedel. J. Ind. Ecol., **2009**. 13(1): p. 154-155.
- [4] A. Fahim, A.E. Dean, M.D.A. Thomas et al., Materials and Corrosion. **2019**. 70(2): p. 328-344.
- [5] J.D. Lee, Concise inorganic chemistry. UK: Blackwell Science Ltd; **2006**.
- [6] Agency for Toxic Substances and Disease Registry (ATSDR), Public Health Service, Toxicological profile for chromium. **2012**.
- [7] B.V. Lenntech, Environmental Effects of Chromium. **2014**.
- [8] C.T. William and B.H. Frank. Role of Chromium in Human Health and in Diabetes. **2014**.
- [9] R.S. Pappas. Metallomics. **2011**. 3(11): p. 1181.
- [10] W.B. Sharon, K.L. Samuel and H.D. Paul. International Programme On Chemical Safety. **1994**.
- [11] Moreno-castilla, Cadmium ion adsorption on different carbon adsorbents from aqueous solutions. **2004**. 20(19): p. 8142-8148.
- [12] C.C. Calgon. History of Activated Carbon. **2014**.
- [13] N. Le-Minh, E. C. Sivret, A. Shammay et al., Critical Reviews in Environmental Science and Technology. **2018**. 48(4): p. 341-375.
- [14] W. J. Thomas and B. Crittenden. Adsorption Technology & Design, **1998**. p. 1-7.
- [15] D. Choudhari, D. Sharma and A. Phadnis. Eur. Chem. Bull. **2013**. 2(11): p. 880-886.
- [16] W. Chandra, S. Chris and H. Hirofumi. Int. J. Eng. Sci., **2012**. 3(1): p. 35-40.
- [17] H. O. Abugu, P.A.C. Okoye, V.I.E. Ajiwe et al., Int. J. Innov. Res. Dev., **2014**. 3(13): p. 418-446
- [18] H. O. Abugu, P.A.C. Okoye, V.I.E. Ajiwe et al., J. Environ. Anal. Chem. **2015**. 2(6): p. 1-17.
- [19] R. Okpuwhara. M.Sc. Thesis. Nigeria: Ahmadu Bello University, Zaria. **2013**.
- [20] Z. Hu and M. Srinivasan. Micropor. Mesopor. Mater. **1999**. 27: p. 11-18.
- [21] E. Abechi, C. Gimba, A. Uzairu et al., Arch. Appl. Sci., **2011**. 3(1): p. 154-164.
- [22] A. A. Ajayi-Banji, A. Temitayo, A.T. Ewemoje et al., Environmental Research, Engineering and Management. **2015**. 71(4): p. 5-10
- [23] A. A. Jalil, S. Triwahyono, M. R. Yaakob et al., Bioresource Technology. **2012**. 120: p. 218-224
- [24] S. Indah, D. Helard and A. Sasmita. Water Science & Technology. **2016**. 73(12): p. 2929-2935
- [25] A. Itodo, F. Abdulrahman, L.G. Hassan et al., Newyork Science Journal. **2010**. 3(5): p. 25-33.
- [26] S. Joshi, M. Adhikari, B.P. Pokharel et al., J. Che Sci, **2013**. 3(5): p. 19 - 24.
- [27] S. Lagergren. Ksver Vetterskapsakad Handligar. **1898**. 24(4): p. 1-39.
- [28] O. A. Ekpete, A. C. Marcus and V. Osi. J. Che., **2017**. 6 pages.
- [29] S. De Gisi, G. Lofrano, M. Grassi & M. Notarnicola. Sustainable Materials and Technologies. **2016**. 9: p. 10-40.
- [30] A. H. Abdullah, A. Kassim, T. Zainal et al., Malaysian J. Anal. Sci. **2000**. 7 (1): p. 65-68.
- [31] H.A, Aziza, M.N. Adlan and K.S. Ariffin. Bioresources Technology. **2008**. 99: p. 1578-1583.
- [32] A. H. Karoyo, L. Dehabadi and L. D. Wilson. ACS Sustainable Chemistry & Engineering, **2018**. 6(4): p. 4603-4613.
- [33] O. A. Ekpete and M. Horsfall Jr., Res J Chem Sci, **2011**. 1(3): p. 10-17
- [34] R.M. Rao, R.R. Bansode, J.N. Losso et al., Bioreources Technology. **2003**. 90: p. 2629-2635.
- [35] L. Aljerf. J Environ Manage. **2018**. 225: p. 120-132.
- [36] J. Rivera-Utrilla, I. Bautista-Toledo, M. Ferro-Gracia et al., Carbon. **2003**. 41: p. 323-330.
- [37] K. Mohanty, M. Jha, B. C. Meikap et al., Chem. Eng. J. **2006**. 117: p. 71.

- [38] T. Nassima and A. Moussa. *Water Practice and Technology*. **2009**. 4(2): p.1-13.
- [39] T. Karthiheyam, S. Rajgopal and L. R. Miranola. *J. Hazard. Mater.* **2005**. 124: p. 192.
- [40] Y.B. Zhan, A. Shukla, S. Shukla et al., *J. Hazard. Mater.* **2000**. 80: p. 33-42.
- [41] A.R. Mohammad, O.F. Mohammad and A.A. Shafiqul. *Dhaka Univ. J. Sci.* **2012**. 60(1): p. 15-20.
- [42] D.W. O'Connell, C. Birkinshaw and T.F. O'Dwyer, *Bioresour. Technol.* **2008**. 99: p. 6709-6724.
- [43] P. Magne and P. L. Walker Jr. Phenol adsorption on activated carbons. **1986**. 24 (2): p. 101.
- [44] J. Coates, In *Encyclopedia of Analytical Chemistry*. **2006**. p. 10815-10837.