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Removal of Chromium (VI) from Aqueous Solution Using Activated Carbon Derived from Modified Bambara Nut Shells (*Vignasubterranea (L.) verdc.)*

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ABSTRACT: Adsorption of Cr (VI) ions from aqueous solution using activated carbon derived from Bambara nut shells (BBNSAC) was investigated using batch adsorption technique. The maximum removal of Cr (VI) ions onto BBNSAC corresponding to 68.00 mg/g was achieved at pH 2, adsorbent dosage 0.01 g and contact time of 60 minute. The Equilibrium data of adsorption revealed that the adsorption of Cr (VI) ions showed better fitting to Langmuir isotherm in comparison to Freundlich, Temkin and Dubinin-Radaushkevich isotherm models. The value of Langmuir monolayer coverage was 55.56 mg/g. However, the kinetics of adsorption was best described by pseudo second-order model with highest correlation coefficient, R^2 value of 0.984. Thermodynamics parameters of adsorption revealed negative value of Gibb's free energy (ΔG) indicating a feasible and spontaneous adsorption process whereas the positive value of change in enthalpy (ΔH) indicates that the adsorption process was endothermic in nature while the positive value of change in entropy (ΔS) revealed that there is an increase in randomness at solid-solution interface during adsorption process.

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Developments in various industrial activities have caused serious threats to the environment as a result of excessive discharge of different toxic substances such as heavy metals and dyes from industrial wastewater (Abdullahi and Nwosu, 2022). Heavy metals are non-degraded materials that occur naturally in the earth crust and usually enter into the body through food, water and air as a result of natural and anthropogenic activities. Chromium is one of the toxic heavy metal released from textile and tannery industries which persist in the environment and accumulate in the living organisms though food chain and eventually leads to serious problems to human (Adebayo *et al*., 2015). Chromium (VI) is known to be toxic and carcinogenic and its long exposure increases the risk of developing cancer in humans, skin allergies and dermatitis (Shadreck and Mugadza, 2013). Continuous exposure to Cr (VI) could also leads to severe respiratory problems such as asthma, bronchitis, cardiovascular and gastrointestinal problems (Bielicka *et al*., 2005). A large number of conventional treatment methods comprising of ion exchange, reverse osmosis and precipitation were used, but adsorption method was found to be the best and promising technique for the treatment of various toxic substances from aqueous solution (Sarkheil *et al.*, 2014). Less expensive adsorbents derived from avocado kernel seeds, sawdust and papaya peels have used for removal of Cr (VI) from aqueous solution. The maximum removal efficiencies of Cr (VI) onto avocado kernel seed, sawdust and papaya peels were found to be 98.18, 96.35 and 94.58 % respectively (Mekonnen *et al*.,

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2015). Kushwaha and Upadhyay (2015) investigated study on removal of chromium using an adsorbent derived from neem sawdust. The finding of the study showed that the maximum removal (84 %) was attained at pH 2. In another study, Nharingo *et al.* (2013) carried out adsorption isotherm studies on biosorption of Cu (II) ions using low cost adsorbent obtained from *Vigna Subterranea* (L.) *Verdc* hull. Themaximum removal was reached at pH 6 with corresponding percentage removal of 61.1 %. The present study is aimed at removal of chromium (VI) ions from aqueous solution using Bambara Nut shells modified with phosphoric acid.

MATERIALS AND METHODS

Preparation of Bambara nut shell activated carbon (BBNSAC): Bambara nut shells (*Vignasubterranea (L.) verdc.)* were obtained from Dawakin- Kudu Town, Dawakin- Kudu Local Government Area Kano State Nigeria (11°50'05''N 8°35'53''E). The shells were washed with de-ionized water to remove all adhered materials and other impurities. The shells were dried at room temperature for two weeks and dried in an oven at 105 °C for 2 hours. The shells were grinded using mortar and pestle and finally sieved to obtain particles of less than 0.5 mm (<500 µm) size.

The preparation of Bambara nut shells activated carbon was done as reported by (Nwosu *et al.*, 2017). A known quantity (50.0 g) of ground Bambara nut shells were impregnated using 100 mL of 2 M phosphoric acid (H_3PO_4). The phosphoric acid impregnated sample were heated in an oven maintained at 110 °C for 7 hours and the carbonization was done using a horizontal tubular furnace in the presence of N_2 that flowed into the reactor at 500 mL/min. The horizontal furnace was first degassed by allowing N_2 to flow into the reactor for 30 minutes.

The pre-treated Bambara nut shells were then carbonized in a horizontal tubular furnace at 400 °C and at a heating rate of 16°C/min under flow of N_2 gas (500 mL/min) for 2 hours. The carbonized samples were allowed to cool at 30 °C under N_2 flow, washed several times with de-ionized water until pH 6-7 was obtained. It was then dried in an oven at 110 °C for 7 hours. The dried samples were stored in an air-tight plastic container for further use.

Batch adsorption: Batch adsorption experiments were investigated to determine the effect of initial concentration, contact time, pH and adsorbent dosage on removal of chromium (VI) ions using phosphoric acid modified adsorbent. The amount of Chromium (VI) ions adsorbed was determined using Eq. 1:

$$\text{Qe} = \frac{(C_0 - Ce\ )V}{M} \qquad (1)$$

Where Qe (mg/g) is the adsorption capacity, C_0 (mg/L) is the initial concentration of Chromium (VI) ions in the solution, Ce (mg/L) is equilibrium concentration of Chromium (VI) ions in the solution, V (L) is the volume of solution used in the flask and M (g) is amount of BBNSAC used.

RESULTS AND DISCUSSION

The physicochemical properties of Bambara nut shell activated carbon (BBNSAC) is presented in Table 1. The percentage yield is ratio of weight of activated carbon to that of the precursor. The yield of activated carbon (BBNSAC) was determined to be 41.67±0.33. The value obtained was in good agreement with the reported yield (41.4 %) for industrial (Raffiea *et al.*, 2012). However, the value obtained was lower than that of activated carbon derived from *Typha orientalis* leaves (62.73 %) (Anisuzzaman *et al.*, 2015).Moisture content indicates the amount water present in the activated carbon and its presence has no significant influence on adsorption capacity (Moyo *et al.*, 2013). Presence of high moisture in the activated carbon usually result in utilizing additional weight of carbon during adsorption process (Adebayo *et al.*, 2015) The moisture content of BBNSAC was 5.99±0.31, lower than the value reported (12.0 %) elsewhere in the literature (Dada *et al.*, 2012).Ash content is the amount of inorganic constituents present in the sample and it usually increases with an increase in carbonization temperature and decrease in the percentage of volatile matter (Gan *et al.*, 2004). The ash content generally has a significant influence on the adsorption capacity, low ash content in the precursor is an indication of good adsorbent and thus leads to better adsorption performance (Anisuzzaman *et al.*, 2015). The ash content of BBNASAC was 8.1±0.01 %. This value lies within the range of ash content (0.2 – 13.4 %) for most of the agricultural products such as rice straw, corn cobs, cotton stalks (Ioannidou and Zabaniotou, 2007).

Table 1: physicochemical properties of BBNSAC

Properties	BBNSAC
Yield (%)	41.67±0.33
Moisture content (%)	5.99±0.31
Ash content (%)	8.10±0.01
Volatile matter (%)	31.30±0.12
Fixed carbon (%)	54.61±0.03
Bulk density (g/cm^3)	0.5I8±0.004
Iodine number (mg/g)	1102.7±8.11
pH	6.87±0.05
Point of zero charge (pHpzc)	6.4

Volatile matter is the amount of combustible matter present in the activated carbon precursor when subjected to a high temperature. Longer carbonization time result in release of more volatiles matter from the char and leads to higher burn off and subsequently lower the carbon yield (Martinez *et al*., 2006). The value of volatile matter in the precursor was 31.3±0.12 %. Volatile matter of (19.8 – 24.5 %) has been reported elsewhere in the literature (Raffiea *et al*., 2012). Fixed carbon indicates the amount of solid combustible residue that is left after volatile matter has been removed from the adsorbent and it was found that the fixed carbon of BBNSAC was 54.61±0.03. Similar value (54.80 %) was reported in the literature study (Kibami *et al*., 2014). The bulk density is an indication of the fiber content of the precursor. The value obtained for BBNSAC was 0.518±0.04 g/cm^3. This value is in good agreement with that of maize tassel based activated carbon (0.52 g/cm^3) (Moyo *et al*., 2013). Iodine number is the measure of activity level of activated carbon. The result obtained indicated that BBNSAC has high iodine number (1102.77±8.11 mg/g). Higher iodine number is an indication of development of microporous structure and higher adsorption ability (Baccar *et al.*, 2009). Iodine number of 901 mg/g has been reported from pilli nut activated carbon (Nwosu *et al*., 2017). pH is measure of acidity or basicity.The result obtained revealed that BBNSAC had a pH of 6.87±0.05, slightly acidic and pH of activated carbon strongly depends on several factors such as method of preparation, surface chemical active groups, inorganic matter content and the type of treatment during manufacturing process (Gan *et al*., 2004). pH of 7.2 was reported from activated carbon derived from stem bark of *Daniellia oliveri* tree(Adegoke *et al*., 2020). The Point of zero charge (pHpzc) is pH at which the net charge on the surface of adsorbent is equals to zero. The pHpzc of BBNSAC was found to be 6.4 which was lower than that of reported value (6.8) in the literature (Adebayo *et al.*, 2015). Generally, when the pH is less than pHpzc, the adsorption of anions is favoured whereas when pH is greater than pHpzc, adsorption of cations is favoured (Govindasmay *et al*., 2009).

*Batch adsorption studies:*Effect of initial concentration: The initial metal ion concentration has a significant influence on the adsorption capacity. The result for the uptake of Cr (VI) ions onto BBNSAC at different concentration is shown in Fig. 1. It could be observed that as the initial concentration increased from 11.6 to 72.46 mg/L, there was corresponding increase in Cr (VI) uptake from 11.93 to 38.93 mg/g. This could be attributed to the availability of adsorption sites at higher chromium (VI) ions in the solution which enhanced the driving force between the aqueous and the solid phase and increases the number of collisions between the metal ions and solid surfaces of the adsorbent thereby causing an increase in uptake capacity (Bohara and Deji, 2018). However, the maximum uptake capacity (40.0 mg/g) for Cr (VI) ions was reached at equilibrium concentration of 48.09 mg/L. Beyond this equilibrium concentration, all the available adsorption sites were occupied and became saturated as such no further uptake of chromium ions was observed with increase in initial concentration (Falih *et al*., 2020). Similar observation was observed on adsorption of Cr (VI) ions from aqueous solution (Gu *et al*., 2018).

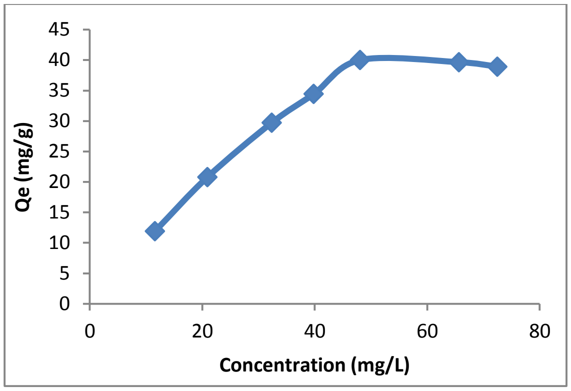


Fig. 1: Effect of initial concentration on adsorption of Cr (VI) ions onto BBNSAC

Effect of contact time: The influence of contact time on Cr (VI) uptake was found to increases as the time of contact varied from 5 - 120 minutes (Fig. 2), but the maximum uptake capacity (37.58 mg/g) was attained at 60 minute. The increase in uptake capacity with time could be due to availability of vacant adsorption sites, but after attaining equilibrium time, all the available binding sites were filled up with chromium (VI) ions which repelled further uptake. This observation is in good agreement with other findings (Goharshadi and Moghaddam 2015).

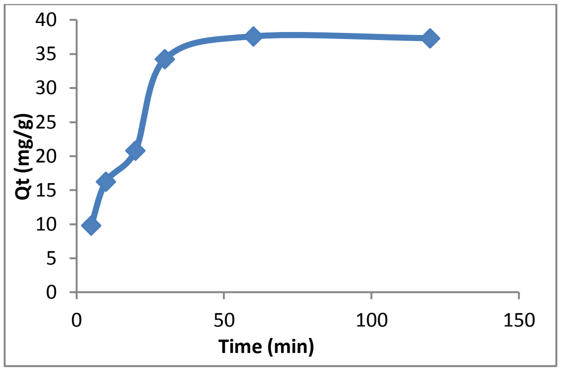


Fig. 2: Effect of contact time on adsorption of Cr (VI) ions onto BBNSAC

*Effect of pH:*The pH of solution strongly affects the uptake of Cr (VI) ions and the result of the influence of pH is shown in Fig. 3. The maximum uptake of Cr (VI) ions was reached at pH 2 which corresponds to uptake capacity of 68.00 mg/g. Chromium (VI) ions in aqueous solution exist in form of oxy-anions such as hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) and their stability depends upon the pH of the system. At low pH (2-6), the predominant form of chromium (VI) is $HCrO_4^-$ while at pH greater than 6, CrO_4^{2-} and $Cr_2O_7^{2-}$ are the most common species (Gu *et al*., 2018; Bohara and Deji, 2018). It could be observed from Table 1 that pH value (6.87) of BBNSAC was greater than its corresponding pHpzc value (6.4) and this indicated that the surface of BBNSAC was negatively charged. Therefore, the maximum uptake of Cr (VI) ions at pH 2 could be attributed to the fact that, at low pH the surface of the adsorbents were saturated with more protons (H+) ions thereby making the surface positively charged and this creates a strong electrostatic force of attraction between the negatively charged chromium oxyanions and the surface of the adsorbent thereby causing an increase in uptake capacity (Das *et al*., 2019). However, as the pH increased, there was a decrease in uptake capacity and this could be due to excess negatively charged hydroxyl ions (OH^-) in the solution which resulted in dual competition of both CrO_4^{2-} and OH^- ions and thus promotes repulsion between the negatively charged surface and oxyanions of chromium (Gupta *et al*., 2010).

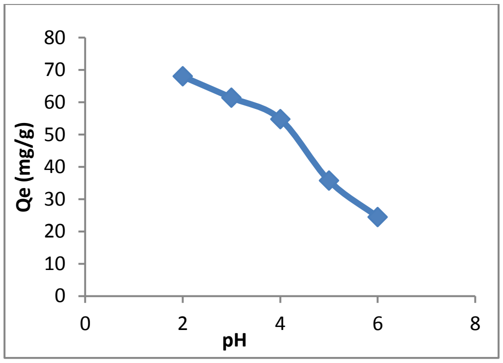


Fig. 3: Effect of pH on adsorption of Cr (VI) ions onto BBNSAC

*Effect of adsorbent dosage:*The influence of adsorbent dosage on uptake of Cr (VI) ions is shown in Fig 4. It was observed that the uptake capacity decreases with increase in adsorbent dosage in which the highest uptake capacity corresponding to 68.0 mg/g was achieved using 0.01 g of BBNSAC adsorbent The decrease in the uptake capacity with increase in adsorbent dosage could be attributed tothe reduction of surface areas of the adsorbent as a result of overlapping of the various adsorption sites (Shukla *et al*., 2000).

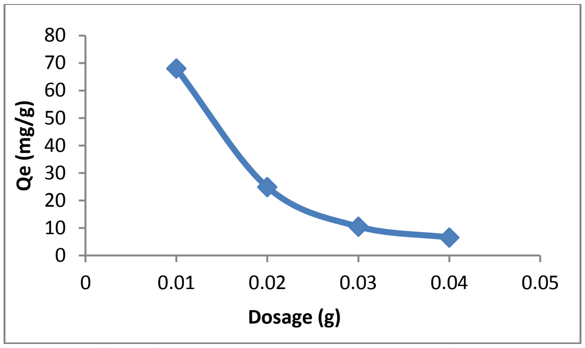


Fig. 4: Effect of adsorbent dosage on adsorption of Cr (VI) ions onto BBNSAC

Effect of temperature: The result for the uptake of Cr (VI) ions onto BBNSAC adsorbent is shown in Fig. 5. As the temperature increases, there was corresponding increase in uptake capacity. This could be attributed to increase in kinetic energy of adsorbent particles thereby promoting strong collision between adsorbent and Cr (VI) ions (Khalid *et al*., 2014). However the highest uptake capacity at 333 k was 37.15 mg/g. A similar trend was observed on adsorption of Cr (VI) ions from aqueous solution (Goharshadi and Moghaddam, 2015).

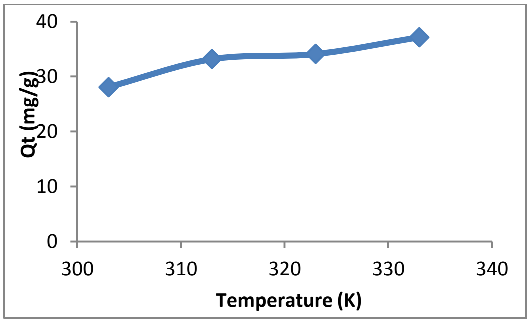


Fig. 5: Effect of temperature on adsorption of Cr (VI) ions onto BBNSAC

Adsorption isotherms:(i) Langmuir isotherm. This is based on the assumption that the adsorption occurs in the form of monolayer and Langmuir equation can be expressed by Eq. 2

$$\frac{Ce}{qe} = \frac{1}{K_L qm} + \frac{Ce}{qm} \qquad 2$$

Where Ce is the equilibrium concentration of Cr (VI) ions (mg/L), qe is the amount of Cr (VI) ions adsorbed per gram of the adsorbent (BBNSAC) at equilibrium (mg/g), qm is the maximum monolayer coverage capacity (mg/g) and K_L is the Langmuir isotherm constant related to the energy of adsorption (L/mg) (Langmuir, 1918). The values of qm and K_L were determined from the slope and intercept of Langmuir plot of $\frac{Ce}{qe}$ against Ce (Fig. 6).

The essential characteristics of Langmuir isotherm can be expressed in terms separation factor (R_L) Eq. (3) which is a dimensionless constant that indicates weather the adsorption process is favorable or not.

$$R_L = \frac{1}{1+K_L C_0} \qquad 3$$

Where R_L is the separation factor, C_o is the initial concentration (mg/L) and K_L is Langmuir adsorption constant

When R_L value is greater than 1 it implies that the adsorption is unfavorable. If R_L value is equal to 1, the adsorption is linear. When R_L value is between 0 and 1, the adsorption is favorable and if R_L value is equal to 0, the adsorption is irreversible (Jain *et al*., 2018).

(ii) Freundlich isotherm. Freundlich isotherm model assumes that the adsorbents have a heterogeneous surface with different adsorption capacity (Freundlich, 1906). Freundlich equation can be express by Eq. 4

$$\log qe = \log K_F + \frac{1}{n}\log Ce \qquad 4$$

Where Ce is the equilibrium concentration of Cr (VI) ions (mg/L), qe is the amount of Cr (VI) ions adsorbed per unit mass of BBNSAC (mg/g), K_F (mg/g) and n (L/mg) are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. Plotting a graph of log qe against log Ce (Fig. 7) gave a straight line graph with slope (1/n) and the intercept Log K_F. When the value of n lies between 1 and 10 it indicates a favourable adsorption process and if the value of 1/n is below 1, it indicates a favourable normal adsorption at low dilution while if the value of 1/n is above 1 it indicates cooperative adsorption or unfavourable adsorption (Adegoke *et al*., 2020).

(iii) Temkin isotherm. This model assumes that heat of adsorption of all molecules in the layer decreases with the surface coverage due to adsorbate-adsorbent interactions and the adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy (Temkin and Pyzhev 1940). Temkin isotherm equation can be expressed by Eq. 5

$$Qe = BIn K_T + BIn Ce \qquad 5$$

Where B = RT/b (J/mol), which is the Temkin constant that is related to heat of adsorption, K_T is the equilibrium binding energy (L/g), R (8.314 J/mol/K) is the universal gas constant and T(K) is the absolute temperature. Plotting a graph of qe against *ln Ce* gave a straight line graph with slope B and intercept K_T (Fig. 8).

(iv) Dubinin-Radushkevich isotherm. This model is generally applied to study the adsorption that occurred onto both homogeneous and heterogeneous surfaces (Dubinin and Radushkevich, 1947). The value of the adsorption energy, E is very useful in predicting whether the adsorption process is physical or chemical in nature (Ghasemi *et al*., 2014). The linearized form of this model is given by Eq 6

$$In qe = In qs - K_{ad}\varepsilon^2 \qquad (6)$$

Where qe is the amount of Cr (VI) ions adsorbed per gram of BBNSAC at equilibrium (mg/g), K_{ad} is a constant related to the mean-free energy of adsorption, qs (mg/g) is the maximum adsorption capacity and ε is the Polanyi potential. The values of qs and K_{ad} can be determined from the plot of *In*qe versus ε^2(Fig. 9) with slope K_{ad} and intercept *In* qs. The Polanyi potential is expressed by Eq. 7

$$\varepsilon = RT\, In\left(1+\frac{1}{Ce}\right) \qquad 7$$

Where R (8.314 J/mol/K) is the universal gas constant and T (K) is the absolute temperature. The value of adsorption energy, E (kJ/mol) can be determined by Eq. 8

$$E = \frac{1}{\sqrt{2K_{ad}}} \qquad (8)$$

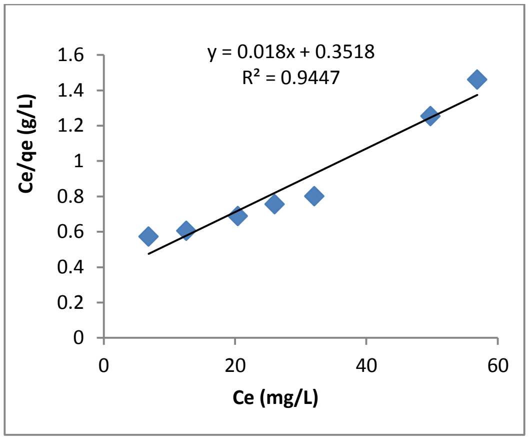


Fig. 6: Langmuir plot on adsorption of Cr (VI) onto BBNSAC

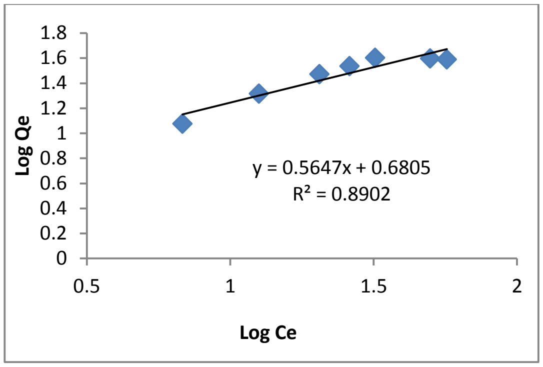
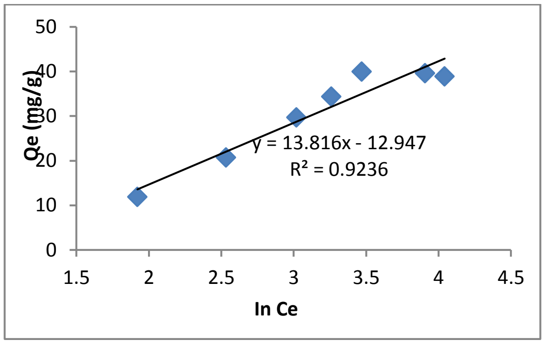


Fig. 7: Freundlich plot on adsorption of Cr (VI) onto BBNSAC



Fi8. 8: Temkin plot on adsorption of Cr (VI) onto BBNSAC

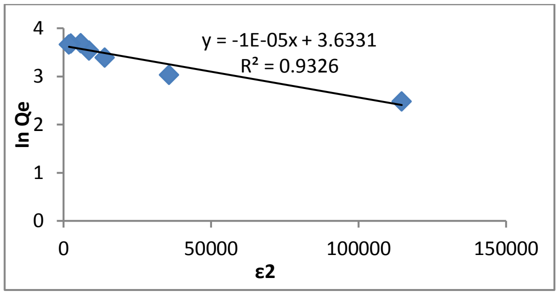


Fig. 9: Dubinin-Radushkevich plot on adsorption of Cr (VI) onto BBNSAC

Table 2 presents the results of adsorption isotherm parameters. It could be observed that the correlation coefficients, R^2 values as indicated in Figs. 6, 7, 8 & 9 were 0.944, 0.890, 0.923 and 0.932 for Langmuir, Freudlich, Temkin and Dubinin- Radaushkevich isotherm models respectively. The value of R^2 obtained from Langmuir model was higher than that of other models and this indicated that the adsorption of Cr (VI) ions onto BBNSAC showed better fitting to Langmuir isotherm. It was also observed from Table 2 that the value of separation factor (R_L) was 0.289 and fell between 0 and 1, thus indicating a favourable adsorption (Timbo *et al*., 2017). The value of Langmuir monolayer coverage, Qm was 55.56 mg/g while Freudlich adsorption capacity, K_F was 4.79 mg/g.

Table 2: Adsorption isotherm parameters on adsorption of Cr (VI) onto BBNSAC

Isotherm model	**Parameter**	**Value**
Langmuir	Qm (mg/g)	55.56
	K_L (L/mg)	0.051
	R_L	0.289
	R^2	0.944
Freundlich	K_F (mg/g)	4.79
	n	1.77
	1/n	0.56
	R^2	0.890
Temkin	B (J/mol)	13.81
	K_T(L/mg)	0.392
	b_T	179.40
	R^2	0.923
Dubinin-Radauskevich	Qs (mg/g)	38.83
	K_{ad} (mol^2/kJ^2)	1×10^{-5}
	E (kJ/mol)	0.224
	R^2	0.932

However, the value of Freundlich

However, the value of Freundlich adsorption intensity (n) was found to be 1.77 which also indicates a favourable adsorption process (Adegoke *et al*., 2020). The value of heat of adsorption, B and Temkin isotherm equilibrium binding constant K_T were 13.81 J/mol and 0.392 L/mg respectively. K_T value of 1.075 L/mg has been reported elsewhere (Dada *et al*., 2012). The value of free energy E, was (0.224 kJ/mol), less than 8 kJ/mol and thus indicating a physical adsorption process (Ozkaya, 2006).

Adsorption Kinetics: (i) *Pseudo-first order kinetics.* Pseudo first-order equation is given by Eq. 9

$$\log(qe - qt) = \log qe - \frac{k_1}{2.303} t \quad (9)$$

where k_1 is the equilibrium rate constant for pseudo-first-order model (min^{-1}), qe and qt are the amounts of Cr(VI) ions adsorbed per gram of BBNSAC (mg/g) at equilibrium and at time t (min), respectively (Lagergren, 1898). A plot of $\log(qe - qt)$ versus time, t (min) gave a straight line graph (Fig. 10). The values of k_1 and qe can be determined from the slope and intercept respectively.

(ii) Pseudo second-order kinetic. Pseudo second-order equation is given by Eq. 10.

$$\frac{t}{qt}=\frac{1}{k_2 qe^2}+\frac{1}{qe}t \qquad (10)$$

Where k_2 is the rate constant for pseudo- second order (g/mg/min), qe and qt are the amounts of Cr(VI) ions adsorbed per gram of BBNSAC (mg/g) at equilibrium and at time t (min) respectively. A plot of t/qt against t gave a straight line graph (Fig. 11). The values of qe and k_2 can be determined from the slope and intercept respectively (Ho and McKay, 1999).

(iii) Elovich kinetic. Elovich equation is given Eq. 11

$$q_t=\frac{1}{\beta}In(\alpha\beta)+\frac{1}{\beta}In(t) \qquad (11)$$

Where α (mg/g min) and β (g/mg) are initial adsorption rate and desorption rate constants respectively. A plot of *qt* versus *lnt* gave a straight line graph (Fig. 12). The values of constant can be obtained from the slope and intercept (Kuipa *et al*., 2014).

(iv) Intra-particle diffusion kinetic. The Intra-particle diffusion mechanism is given by Eq. 12

$$qt=K_{id}\,t^{1/2}+C \qquad (I2)$$

Where k_{id} and C are the intra-particle diffusion rate constant and boundary layer thickness respectively. According to this model, if the plot of qt against $t^{1/2}$ is linear, then intra-particle diffusion is involved in the adsorption process and if the plot passes through the origin it indicates that intra-particle diffusion is the sole rate-limiting step. However, when the plots do not pass through the origin is an indication of some degree of boundary layer control (Weber and Morris, 1963). The values of constant can be obtained from the graph and intercept (Fig. 13).

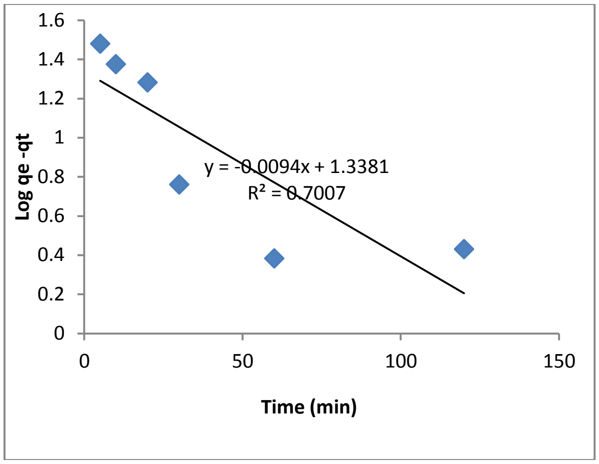


Fig. 10: Pseudo first -order plot on adsorption of Cr (VI) onto BBNSAC

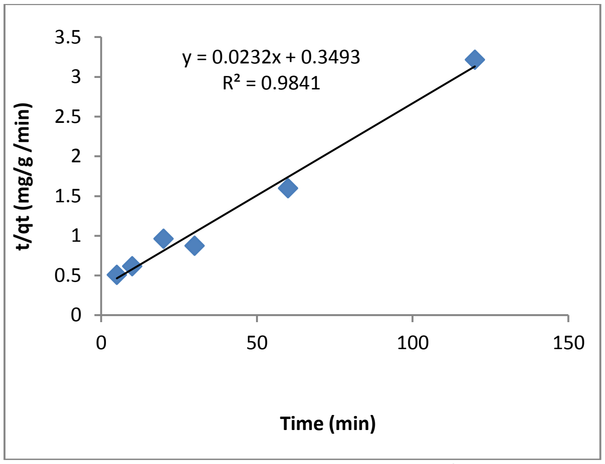


Fig. 11: Pseudo second-order plot on adsorption of Cr (VI) onto BBNSAC

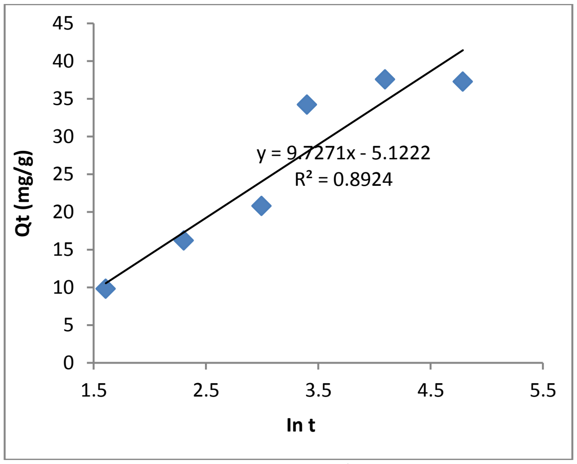


Fig. 12: Elovich plot on adsorption of Cr (VI) onto BBNSAC

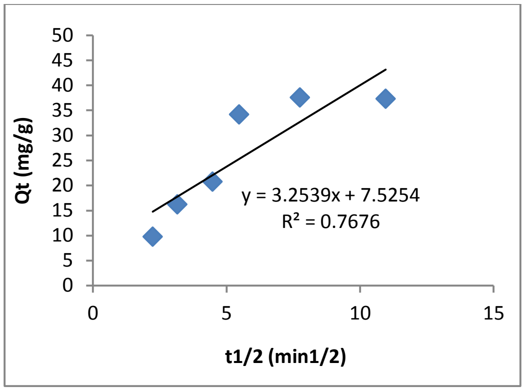


Fig. 13: Intra-particle diffusion plot on adsorption of Cr (VI) onto BBNSAC

Table 3: Kinetic parameters on adsorption of Cr (VI) onto BBNSAC

Kinetic model	Parameter	Value
Pseudo first-order	Qe Cal. (mg/g)	21.78
	Qe Exp.(mg/g)	40.00
	K_1 (min^{-1})	2.07×10^{-2}
	R^2	0.700
Pseudo second-order	Qe Cal. (mg/g)	43.48
	Qe Exp.(mg/g)	40.00
	k_2 (g/mg min^{-1})	1.52×10^{-3}
	R^2	0.984
Elovich	α (mg/g min)	5.728
	β (g/mg)	0.103
	R^2	0.892
Intra-particle	K_{id} (mg/g $min^{1/2}$)	3.25
	C	7.53
	R^2	0.767

The adsorption kinetic parameters on adsorption of Cr (VI) ions onto BBNSAC are presented in Table 3. The value of correlation coefficients, R^2 were 0.700, 0.984, 0.892 and 0.767 for pseudo first order, pseudo second-order, elovich and intra-particle models respectively. The linearity of the plots with high R^2 value close to unity is an indication of the applicability of the model and R^2 value (0.984) obtained using pseudo second-order model indicates that the kinetic of adsorption fitted best to pseudo second-order model than any other model which is based on the assumption that the rate limiting step is chemisorptions involving valence forces by sharing or exchange of electrons between the adsorbate and adsorbent (Pathania *et al.*, 2017). The values of Qe calculated (43.48 mg/g) and that of Qe experimental (40.00 mg/g) obtained from pseudo second-order model were in good agreement with each other unlike that of pseudo first-order model. This also suggested that the kinetic of adsorption was well described by pseudo second-order. A similar observation was reported (Nwosu *et al.* 2017; Olajire *et al.*, 2015). The value of initial adsorption rate constant, α (5.728 mg/g min) was relatively high which is an indication that the adsorbent (BBNSAC) had a greater tendency and ability to adsorbed Cr (VI) ions (Hanafiah *et al.*, 2021). The value of boundary layer thickness, C gives an idea about the thickness of the boundary layer. The larger the intercept, the greater the boundary effect or greater the contribution of the surface adsorption in the rate-determining step (Mahmoodi *et al.*, 2011). It was found that the value of C was 7.53 and this showed that some other mechanism in the adsorption processes were involved together with the intra-particle diffusion. Boundary layer thickness of 127.73 has been reported (Kuang *et al.*, 2020).

Adsorption thermodynamics: Thermodynamic parameters on adsorption of Cr (VI) ions onto BBNSAC such as change in Gibbs free energy (ΔG) enthalpy change (ΔH), and entropy change (ΔS) were determined from Eqs. (13), (14) and (15):

$$\Delta G = -RT\,In\,Kc \qquad (13)$$

$$InKc = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (14)$$

$$\Delta G = \Delta H - T\Delta S \qquad (15)$$

Where T is the absolute temperature (K), R is the ideal gas constant (8.314 J/mol/K), Kc is the distribution coefficient. The values for ΔH and ΔS can be determined from the slopes and intercepts of the Van't Hoff plot of *lnKc* versus 1/T (Fig. 14) (Adebayo *et al.*, 2015).

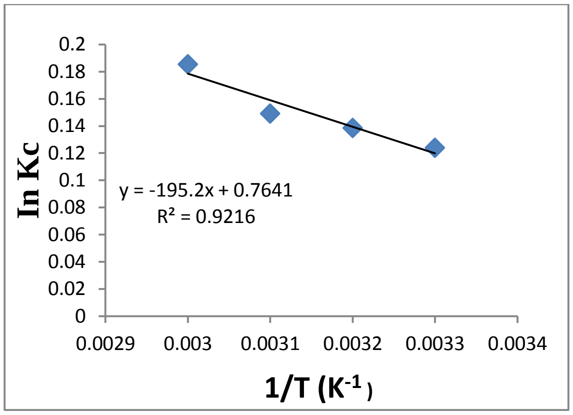


Fig. 14: Thermodynamic plot on adsorption of Cr (VI) onto BBNSAC

Table 4: Thermodynamic parameters on adsorption of Cr (VI) ions onto BBNSAC

Adsorbent	**Temp. (K)**	**ΔG(kJ/mol)**	**ΔH (kJ/mol)**	**ΔS (J/mol /K)**	**R^2**
BBNSAC	303	- 1.93	1.62	6.35	0.921
	313	- 1.99			
	323	- 2.05			
	333	- 2.12			

Table 4 presents the values of thermodynamic parameters. It could be observed that the negative values of Gibb's free energy, ΔG as the temperature increased from 303 to 333 K increased from -1.93 to -2.12 kJ/mol indicting that the adsorption of Cr (VI) ions onto BBNSAC was feasible and spontaneous in nature. The positive values of enthalpy change (1.62kJ/mol) and entropy change (6.35 J/mol/K) revealed endothermic process and increased in randomness at solid-solution interface. Similar observation has been reported (Orimolade *et al*., 2018).

Conclusion: This study showed that activated carbon derived from Bambara nut shells using chemical activation with phosphoric acid has been successfully used as less expensive adsorbent for effective removal of Cr (VI) ions from aqueous solution. The study further revealed that Langmuir isotherm model and pseudo second-order kinetic model described the adsorption isotherm and adsorption kinetics respectively. However, thermodynamic parameters revealed endothermic, feasible and spontaneous adsorption process.

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