Adsorption Studies of Cr (VI) ions onto Hematite, Activated Carbon and their Composite

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Abstract
Water pollution by heavy metals has become a major environmental issue. The present work investigated the adsorptive removal of hexavalent chromium from aqueous solution on the three adsorbents, Hematite (HEM), *Moringa oleifera* pod activated carbon (MAC) and their composite (HEMAC). The adsorption of Cr (VI) ions was conducted using batch experimental method. The effect of initial metal ions concentration (25-250 mg/L), adsorbent dosage (0.01 to 0.05 g), contact time (30-180 min), pH (2-8) and temperature (303-343 K) on the adsorption capacity of these adsorbents were evaluated and optimized. The Cr (VI) ions at an initial concentration of 200 mg/L gave the maximum adsorption capacity of 7.27 mg/g, 7.33 mg/g and 12.02 for HEM, MAC and HEMAC respectively. The equilibrium data obtained from the adsorption studies was fitted using the Langmuir, Freundlich and Temkin isotherm models, the adsorption process was best described by the Temkin isotherm model. The kinetic and thermodynamic studies revealed that the prepared Hematite and activated carbon are efficient adsorbents and the *Moringa oleifera* pod activated carbon gave a more favourable adsorbent for the removal of heavy metal in waste water.

Keywords: Adsorbent, Isotherm, Kinetics, Thermodynamics, Equilibrium

Introduction
Hygienic and sufficient fresh water is required for the existence of all living organisms as well as the efficient maintenance of the environment. Untreated effluents containing toxic heavy metals are being discharged at an alarming rate into water bodies as a result of the increased use of heavy metals in various industrial operations such as smelting, mining, and electroplating (Wang *et al*., 2020). Heavy metals are not biodegradable and pose a serious threat to human's health because they are accumulated in the food chain. For instance, adverse effect of cadmium exposure includes hypertension, renal disorder, damages to kidney, lungs and other vital organs in the body (Baohong *et al*., 2019).

Hexavalent chromium is another toxic heavy metal found in the effluents of electroplating, leather tanning, mining, textile and fertilizer industries. It is toxic to human beings and animals. The maximum permissible limit for hexavalent chromium in drinking water is 0.05 mg/l (Levankumar, 2009).

As a result of their detrimental effects, it is very important to remove heavy metals from the aqueous system. Therefore, several methods have been employed to solve this problem including coagulation, membrane filtration, ion exchange, chemical precipitation, adsorption, electrochemical treatment etc. (Anamika *et al*., 2020). But most of these methods are expensive, generate toxic waste by-product and their inability to

remove toxic heavy metals at ppm or ppb level. However, adsorption has proven to be practicable, convenient and effective technique due to its low cost and simple operation. A wide variety of adsorbents for adsorption process have been developed and evaluated for the treatment of polluted water such as activated carbon from different sources, biomaterials, metal oxides, polymeric adsorbents, hybrid materials, carbon nanotubes etc. (Li *et al*., 2019).

Iron oxide is one of the common minerals in natural environment. It has relatively high surface area, surface charges and regulates the concentrations of metal ions and organic matter in soil and aqueous systems through the process of adsorption (Debnath *et al*., 2016). Hematite is a type of iron oxide which crystallizes in the rhombohedral system. Weathering causes magnetite to change into hematite while retaining its crystal and cubic shape. This type of hematite is called maghemite (Khorshidi and Azadmehr, 2016). Its colour ranges from grey to black, blood red in thin fragment and streak is dull red (Adegoke *et al*., 2014).

As a result of the large pore size of activated carbon and the greater surface area per unit mass of metal oxides such as hematite and magnetite, the attention of researchers was drawn to improve its application in waste water treatment, as composite adsorbents enhance the efficiency of the adsorption process. In this study, hematite, activated carbon obtained from *Moringa oleifera* pod, and their composite was applied for the removal of Cr (VI) ions from aqueous solution.

Materials and Methods
Sample Collection and Preparation
The moringa seed pod were collected from Moje College of Education Agricultural Research Institute, Erin-Ile Kwara State. The pod was thoroughly washed with deionized water and oven-dried at 80 ºC for 8 hr. This was then followed by carbonization and activation with 600 ml of 10 % NaOH (w/v) for 24 hr (Arunkumar *et al*., 2014)

Preparation of Hematite- Activated Carbon Composite Mixture

40 g of $Fe(NO_3)_3.9H_2O$ was dissolved in 500 ml of preheated deionized water to 90 ºC which was then added to 300 ml of 1 M KOH preheated to 90ºC to form a precipitate. After 2 min, 50 ml of 1 M $NaHCO_3$ was added. Then, 12 g of moringa oleifera pod activated carbon (MAC) was added to the mixture to produce hematite–activated carbon (HEMAC 1:2) in the ratio 1:2 composite mixture. The precipitate formed was then held in a closed polythene flask at 90 ºC for 48 hr in an oven, filtered and washed several times with deionized water until pH of the filtrate of about 8-9 was achieved (Schwertmann and Cornell, 2007).

Preparation of Stock Solution of Cr (VI) ions
Chromium (VI) stock solution of 1,000 mg/L was prepared by dissolving 2.826 g of $K_2Cr_2O_7$ in deionized water and making up to 1000 ml mark of the standard flask. The solution pH was adjusted to a pH of 2 as observed from the speciation diagram for chromium. The working solutions (25–300 mg/L) were prepared by serial dilution. The concentrations of the working solutions were determined on a ultraviolet–visible spectrophotometer at a predetermined wavelength of maximum absorption of the adsorbate (Abdus-Salam and Adekola, 2005).

Adsorption of Cr (VI) ions from Aqueous Solution
Batch adsorption experiments was carried out to investigate the effects of initial metal ion concentration, adsorbent dose, contact time, pH and temperature on the adsorption of Cr (VI) on each adsorbents (hematite, activated carbon and the composite). A 20 ml of the working solutions with initial concentrations varying from 25-300 ppm was measured into 100 ml conical containing 0.05 g of the adsorbents. The mixture was agitated on a mechanical shaker for 180 min at a fixed temperature and agitation speed of 250 rpm. After the equilibrium time was attained, the supernatant liquids were filtered and the un-adsorbed Cr (VI) ions in the filtrates were analyzed using UV–visible spectrophotometer. The amount of Cr (VI) ions adsorbed was calculated from Equation (1).

$$q_e = \frac{C_{o-C_f}}{m} \times v \qquad (1)$$

The percentage of metal ions adsorbed from aqueous solution was calculated using the equation (2) below.

$$\% \text{ Adsorption} = \frac{c_o - c_f}{C_o} \times 100 \qquad (2)$$

Where q_e is the quantity of metal adsorbed (mg/g), C_0 and C_f are the initial and final concentration of metal ions in the solution at any time in (mg/l), V is the total volume of the metal standard solution in the flask (L), and m is the mass of adsorbent used in (g).

Batch Adsorption Process

Effect of Initial Concentration

A 20 ml of 25, 50, 100, 150, 200 and 250 mg/L of Cr (VI) ions concentrations were prepared by serial dilution of the stock solution, contacted separately with 0.05 g of hematite (HEM), *Moringa oleifera* pod activated carbon (MAC) and their composite at 30ºC for 3 hr and agitated on a mechanical shaker at 250 rpm. After the set time of shaking has elapsed, the mixtures were filtered. The unadsorbed Cr (VI) ions in the filtrate were analyzed using UV-Visible spectrophotometer. The quantity adsorbed, q_e, was calculated from Equation 1.

Effect of Adsorbent Dosage

A 20 ml of the 200 mg/L of the Cr (VI) ions was contacted with varying amounts of the adsorbents (0.01, 0.02, 0.03, 0.04 and 0.05 g) in a well labeled 100ml conical flask with cork. The mixture was shaken on a mechanical shaker for 3 hr at agitation speed of 250 rpm. The resultant solutions were filtered and the filtrate was analyzed for the unadsorbed metal ions using UV-Visible spectrophotometer at a predetermined wavelength of maximum absorption of each of the adsorbate. The quantity adsorbed, q_e, was calculated from equation 1.

Effect of Contact Time

A 0.01 g of HEM, MAC and HEMAC was weighed separately in 100 ml conical flasks containing 20 ml of 200 mg/L of the adsorbate. The mixture was agitated on a mechanical shaker at 250 rpm at room temperature within the time intervals of 30, 60, 90, 120,150 and 180 minutes. At the completion of the chosen contact times, the solutions were filtered and analyzed for q_e using UV-Visible spectrophotometer.

Effect of pH

The effect of pH on adsorption of Cr (VI) ions was studied over the pH range of 2-8. A 20 ml of the 200 mg/L of metal ions was contacted with 0.01 g of HEM, MAC and HEMAC in 100 ml conical flask. The solutions were equilibrated at 250 rpm and optimum contact time. The resultant solutions were filtered and the residual metal ion concentrations were analyzed using UV-Visible spectrophotometer. The q_e was calculated from equation 1.

Effect of Temperature

The Temperature was varied between 30 and 70 ºC (30, 40, 50. 60 and 70 ºC). A 20 ml of the optimum concentration of Cr (VI) ions was contacted with 0.01 g of the adsorbents at the optimal pH of solution and agitation time. The mixtures were equilibrated at the optimum contact time and aforementioned temperatures. The mixtures were filtered and analyzed for unabsorbed Cr (VI) ions with the aid of UV-Visible spectrophotometer.

Adsorption Isotherm, Kinetics and Thermodynamics

The adsorption isotherms are important in the study and design of the adsorption systems. The Langmuir, Freundlich and Temkin Isotherm models were applied to describe the adsorption of Cr (VI) ions on Hematite (HEM), *Moringa oleifera* pod activated carbon (MAC) and their composite (HEMAC). The linear form of the equation of these models are presented below;

Langmuir: $\dfrac{C_e}{q_e} = \dfrac{1}{K_L \, q_m} + \dfrac{1}{q_m} C_e \qquad (3)$

Freundlich: $\text{Log } q_e = Log\, K_f + (\frac{1}{n}) \text{ Log } C_e \quad (4)$

Temkin: $\quad q_e = \quad$ B In A + B In $C_e \quad$ (5)

Where C_e(mg/L) is the adsorbate concentration at equilibrium, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_{max} (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant related to the energy of adsorption; K_f and n are Freundlich constants, K_f determines the binding capacity of the adsorbent and n describes the affinity between

the adsorbent and metal ions (Labied *et al.*, 2018). A and B are the Temkin Isotherm constants; A is the equilibrium binding constant [Lg^{-1}] corresponding to the maximum binding energy and B is related to the heat of adsorption.

Kinetic models are often employed to determine the rate of the adsorption process and the potential rate controlling mechanism. The results obtained from the study of the effect of contact time on the adsorption process were fitted into pseudo-first-order and pseudo-second-order kinetic models and the equations are stated as follows:

Pseudo-first-order: In $(q_{e-}q_t)$ = In q_e- k_1 t (6)

Pseudo-second-order: $\frac{t}{q_t} = \frac{1}{k_{2}q_e^2} + \frac{1}{q_e} t$ (7)

where q_e and q_t are the amounts of Cr (VI) ions adsorbed (mg/g) at equilibrium and at time t (min), K_1 (min^{-1}) is the rate constant of the pseudo-first-order kinetic model and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order kinetic model.

The thermodynamic parameters such as changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined to understand the effect of temperature on the adsorption process. The values of these parameters were evaluated from the equations (8, 9 and 10)

$$K_c = \frac{C\,A_e}{C_e}$$ (8)

$$\Delta G^o = -RT \ln K$$ (9)

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H^o}{RT}$$ (10)

Where K_c is the equilibrium constant, C_e(mg/L) is the equilibrium concentration of adsorbate in solution (mg/L), CA_e (mg/L) is the equilibrium solid-phase concentration. R is the gas constant (8.314 J/mol/K) and T is the temperature (K).

Results and Discussion

Adsorption Experiment Results: Effect of Initial Concentration

It can be observed from Fig. 1 that the adsorption capacity of hematite (HEM), *Moringa oleifera* pod activated carbon (MAC) and their composite (HEMAC) increases with increase in initial concentration of Cr (VI) ions. The HEMAC exhibits a greater adsorption capacity than HEM and MAC. Similarly, MAC showed a higher adsorption capacity for Cr (VI) ions removal than HEM. The extent to which adsorption take place in a particular adsorption system is a function of initial concentration of the adsorbate (Ahalaya, 2005). The observed trend can be attributed to an increase in the driving force of adsorption which increases with the concentration gradient of the metal ions (Liu *et al.*, 2019). Similar results were reported by Mondal and Chakraborty, (2020).

From Figure 1, HEMAC showed a higher adsorption capacity for Cr (VI) with 12.02 mg/g in comparison with MAC (7.33 mg/g) and HEM (7.27 mg/g). It can be deduced from the plots that the trend of the adsorption capacity of the three adsorbents is in the order of HEMAC > MAC > HEM.
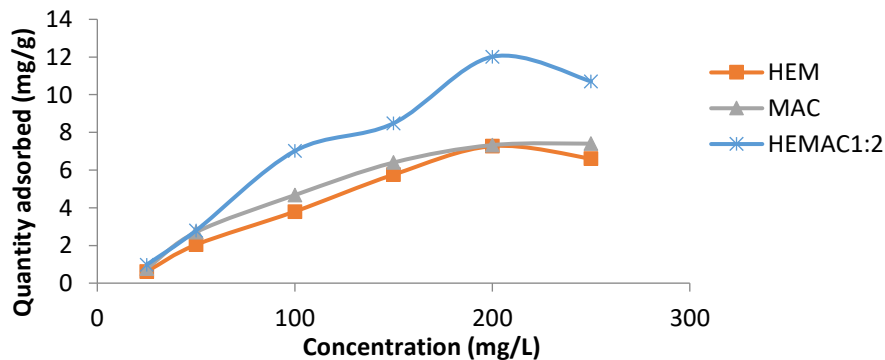

Figure 1: Effect of initial concentration on Adsorption of Cr (VI) ions

Effect of Adsorbent Dosage

The effect of the adsorbents dosage on the adsorption of Cr (VI) ions is depicted in Figure 2. The quantity adsorbed decreased with an increase in the dosage of HEM, MAC and HEMAC. This decrease in adsorption capacity can be due to the overlapping of the adsorption sites on the adsorbent which resulted into an increase in the diffusion path length (Etim, 2016). It was observed that as the adsorbents dose increased from 0.01 to 0.05 g the quantity adsorbed (mg/g) decreased from 13.16 mg/g to 5.69 mg/g for adsorption of Cr (VI) on HEM, 12.75 mg/g to

9.73 for Cr (VI) on MAC and from 18.24 mg/g to 13.1 mg/g for Cr (VI) on the composite. Increasing the adsorbents dose beyond 0.03 g made little or no practical change to the quantity of Cr (VI) adsorbed. Similar trend was reported in the literature where adsorption capacity for Cr (VI) removal decreases with increasing adsorbent dosage (Adebayo *et al*., 2020; Jaiswal *et al*., 2013). It was observed that small amount of adsorbent gave maximum adsorption, this may be attributed to the availability of high surface area and micropore volume of the adsorbents.
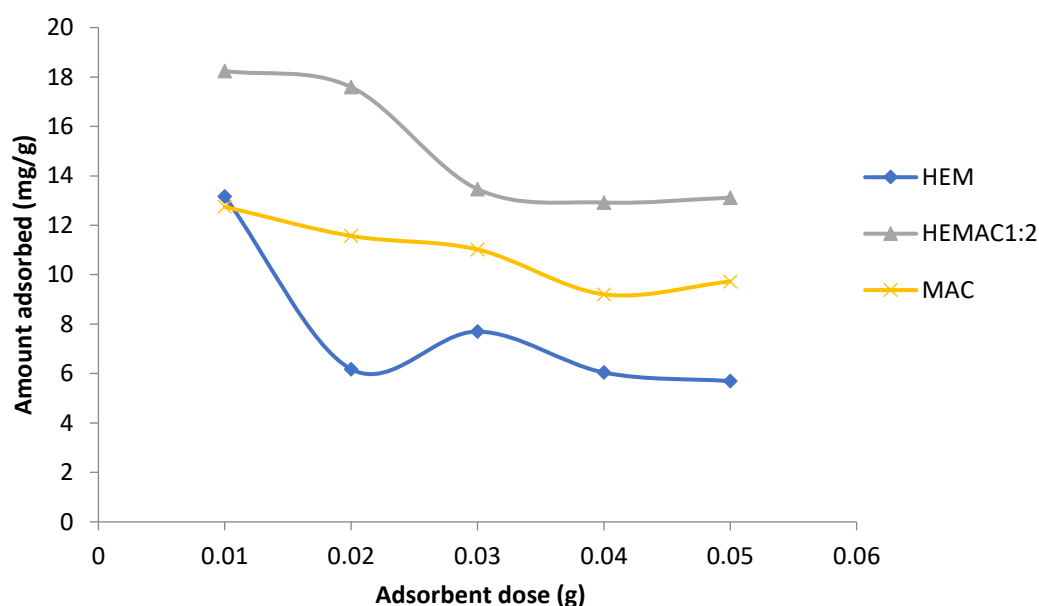

Figure 2: Effect of Adsorbent Dosage on Adsorption of Cr(VI) on Adsorption of Cr (VI) ions

Effect of Contact Time

The effect of contact time on the adsorption of Cr (VI) on HEM, MAC and HEMAC is shown in Figure 3. It was observed that the amount of metal ions adsorbed increases with increase in contact time to the peak when equilibrium was reached at 140 min for HEM, 160 min for MAC and 100 min for HEMAC with the adsorption capacity of 23.45 mg/g, 32.53 mg/g and 40 mg/g respectively. Contact time is one of the

important factors that determines the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). It is obvious from Fig. 3 that the adsorption process was in two stages. The first initial rapid stage which was due to the large initial concentration gradient between the metal ions in the solution and the number of available vacant sites on the adsorbent surface (Abdus-Salam and Adekola, 2018) and followed by the slow stage which was a diffusion-controlled stage.
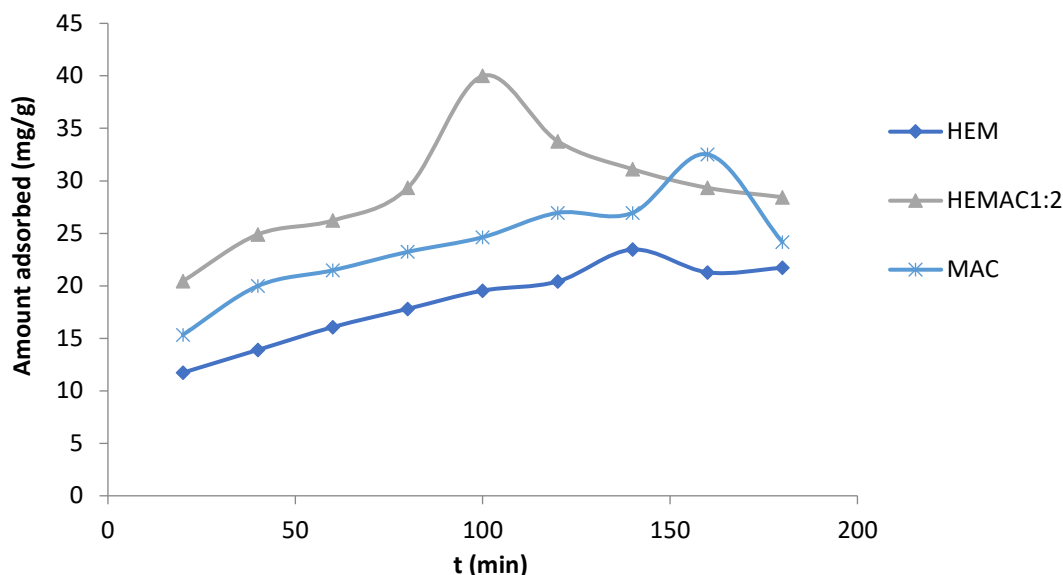
Figure 3: Effect of Contact Time on Adsorption of Cr (VI) ions

Effect of Temperature

Temperature is one of the important factors which directly influence the mobility and transfer of metal ions in aqueous solution (Wang *et al*., 2019)**.** The effect of temperature on the adsorption of Cr (VI) ions onto the three adsorbents was studied by varying the temperature between 303-343 K. It was observed from Fig. 4 that the adsorption capacity of HEM, MAC and HEMAC increases with a rise in temperature from 303 K to 313 K after which a further increase in temperature resulted to a slow adsorption of metal ions. Maximum adsorption capacity was achieved at 313 K for HEM, MAC and HEMAC with values of 43.78 mg/g, 49.24 mg/g and 55.79 mg/g respectively. The decrease in adsorption capacity with increase in temperature indicate a weak interaction between the metal ions and the adsorbents. At high temperature, the thickness of the boundary layer decreases due to the increased escape tendency of the Cr (VI) ions from the surface of the adsorbents to the bulk solution which resulted to decrease in adsorption of metal ions (Horsfall and Spiff, 2005)
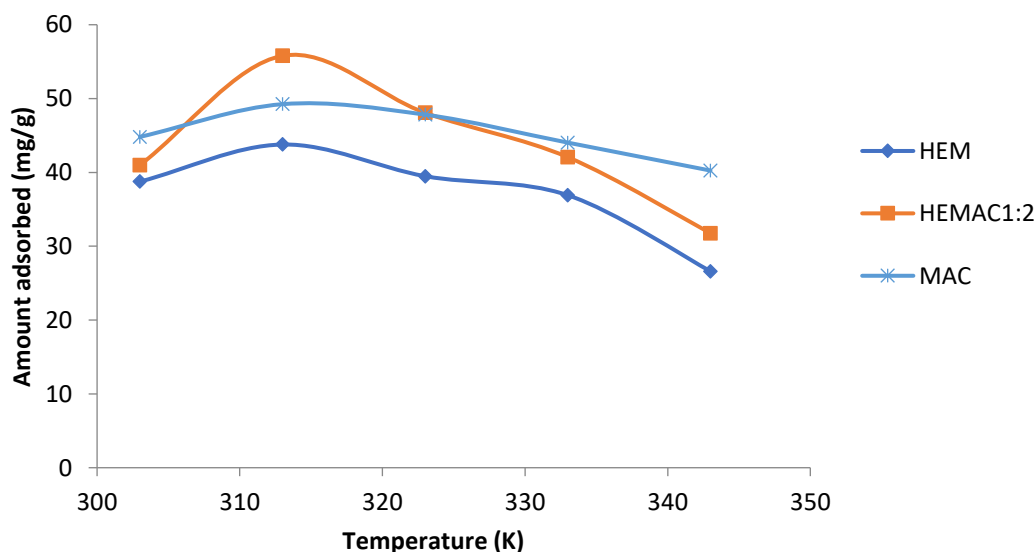

Figure 4: Effect of Temperature on Adsorption of Cr (VI) ions

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Effect of pH

The results of effect of pH on adsorption of Cr (VI) ions on HEM, MAC and HEMAC are presented in Fig. 4. It was observed that the amount of Cr (VI) ions adsorbed from aqueous solution was low at low pH values and increased with increasing pH of the solution for HEM, MAC and HEMAC. Maximum removal of Cr (VI) was observed at pH of 8 for the three adsorbents.
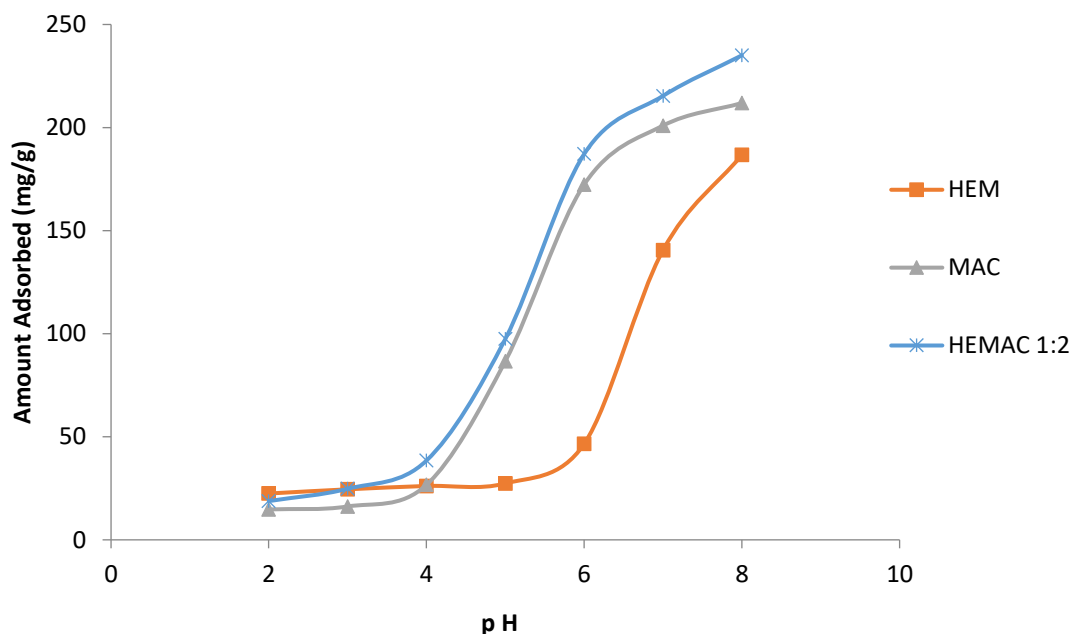

Figure 5: Effect of pH on Adsorption of Cr (VI) ions

Adsorption Isotherm

The Three isotherm models (Langmuir, Freundlich and Temkin) were applied for the treatment of equilibrium data obtained from the adsorption studies. The isotherm parameters obtained for the various adsorption systems are presented in Table 1. The Temkin Isotherm model had the best fittings with R^2 values of 0.96, 0.99 and 0.91 respectively for the adsorption of Cr (VI) ions on HEM, MAC and HEMAC. The best fittings of the experimental data into the Temkin isotherm model are in the descending order: MAC>HEM>HEMAC.

The Temkin adsorption equilibrium binding energy constant, 'A' values calculated are 0.048, 0.056 and 0.042 and the 'B' values are 2.952, 3.023 and 5.304 respectively for the adsorption of Cr (VI) on HEM, MAC and HEMAC. These low values of the binding energies and heat of adsorption of the systems indicate physical adsorption. The values of the equilibrium binding energy constant, 'A' shows that MAC had the highest adsorption potential for Cr (VI) ions removal, followed by HEM while HEMAC had the least potential.

However, from the Freundlich Isotherm model, the value of 1/n was 1.044, 0.847 and 0.943 for the HEM, MAC and HEMAC respectively. The smaller the value of 1/n, the greater the extent of heterogeneity (Dada *et al*., 2010). On this basis, the interaction between the adsorbent-adsorbate system is in the order of MAC> HEMAC > HEM. The R^2 value of 0.0048, 0.172 and 0.1443 obtained from the Langmuir Isotherm plot of HEM, MAC and HEMAC showed that the equilibrium data did not fit well into the Langmuir Isotherm model.

Table 1: Isotherm Parameters for the Adsorption of Cr (VI) ions on HEM, MAC and HEMAC

Isotherm Model	Parameters	HEM	MAC	HEMAC
Langmuir	q_m (mg/g)	169.491	31.949	31.949
	K_L (L/mg)	0.00018	0.0015	0.00271
	R_L	0.965	0.727	0.649
	R^2	0.0048	0.172	0.443
Freundlich				
	K_F (L/mg)	0.03	0.0562	0.134
	n	0.958	1.06	1.282
Temkin	1/n	1.044	0.943	0.847
	R^2	0.941	0.912	0.901
	B (j/mol)	2.952	3.023	5.304
	b_o	839.28	819.57	467.11
	A (L/mg)	0.048	0.056	0.042
	R^2	0.957	0.990	0.914

Adsorption Kinetics

In order to further understand the effect of contact time on the adsorption process, the kinetic data was fitted into the Pseudo-first-order and Pseudo-second-order models. Based on the R^2 values obtained from all the adsorption systems (Table 2), the Pseudo-second-order model gave a better description of the adsorption process than the Pseudo-first-order Model. Also, the good agreement between the experimental and calculated q_e values for the adsorption of Cr (VI) on the three adsorbents confirms the suitability of Pseudo-second-order model for the description of the mechanism of the adsorption process. This indicates that the mechanism of the adsorption process involved chemisorption reaction which may be the rate-limiting step (Abdus-Salam and Adekola, 2018).

Table 2: Kinetic Parameters for Adsorption of Cr (VI) ions on HEM, MAC and HEMAC

	Pseudo-first-order			**Pseudo-second-order**			
Adsorbent	$K_1(min^{-1})$	$q_e\ cal\ (\frac{mg}{g})$	R^2	$K_2(\frac{g}{mgmin})$	$q_e\ exp\ (\frac{mg}{g})$	$q_e\ cal\ (\frac{mg}{g})$	R^2
HEM	0.013	15.689	0.849	1.207×10^{-3}	23.453	26.312	0.982
MAC	0.010	19.670	0.470	1.566×10^{-3}	32.528	31.25	0.933
HEMAC	0.003	12.769	0.056	7.037×10^{-3}	40.000	32.26	0.951

Thermodynamic studies

The determination of thermodynamic parameters is important to evaluate the orientation and feasibility of physicochemical adsorption process. The results obtained from the study of the effect of temperature on the adsorption process were used to predict the nature of the adsorption process of Cr (VI) ions on HEM, MAC and HEMAC composite. The thermodynamic parameters such as the change in enthalpy, entropy change and the change in the Gibb's free energy of the adsorption process were determined using equations 8, 9 and 10. Table 3 shows the thermodynamic parameters ΔG, ΔS and ΔH computed from In K_c against $1/T$. The negative values of ΔH that ranges between -8.447 and -2.969 kj/mol for the three adsorbents indicate an exothermic adsorption process which implies that the adsorption capacity decreases with an increase in temperature. The negative values of ΔS for the adsorption of Cr (VI) ions on HEM, MAC

and HEMAC revealed an enthalpy driven adsorption process, it also shows that no significant change occurs in the internal structures of the adsorbent during the adsorption process (Saha and Chowdhury, 2011). The values of ΔG were positive for

the three adsorbents suggesting that the adsorption processes are not spontaneous and require some energy from an external source to enhance the removal of metal ions (Saha and Chowdhury, 2011).

Table 3: Thermodynamics Parameters for the Adsorption of Cr (VI) ions onto HEM, MAC and HEMAC

Adsorbent	ΔH (kj/mol)	ΔS (j/mol/k)	ΔG (kj/mol)				
			303 K	313 K	323 K	333 K	343 K
HEM	-8.447	-39.51	3.877	3.652	4.078	4.41	5.556
MAC	-2.969	-22.656	4.093	3.958	4.172	4.552	4.969
HEMAC	-7.265	-34.35	3.721	2.931	3.485	4.009	5.012

Conclusion

From the present study, it can be concluded that the hematite particles (HEM), *Moringa oleifera* pod activated carbon (MAC) and hematite-activated carbon composite (HEMAC) have the potential for the adsorption of Cr (VI) ions from aqueous solutions. However, *Moringa oleifera* pod activated carbon (MAC) performed best. The adsorption process was greatly influenced by the initial metal ion concentration, adsorbent dose, contact time, temperature and pH. The Langmuir, Freundlich and Temkin isotherm models were employed to describe the adsorption of hexavalent chromium onto the three adsorbents of which the Temkin isotherm model fitted best. The kinetic of the adsorption process was well explained by pseudo-second-order kinetic model indicating that chemisorption was the rate limiting step. The thermodynamics studies revealed that the adsorption of Cr (VI) ions was exothermic and enthalpy driven process.

References

Abdus-Salam, N. and Adekola, F. A. (2005). The influence of pH and Adsorbent Concentration on Adsorption of Lead and Zinc on a Natural Goethite. *African Journal of Science and Technology (AJST).*6(2): 55-66.

Abdus-Salam, N., and Adekola, S. K. (2018). Adsorption studies of zinc (II) on magnetite, baobab (*Adansonia digitata*) and magnetite–baobab composite. *Applied Water Science*. 8(8): 1-11.

Adebayo, G. B., Adegoke, H. I., andFauzeeyat, S. (2020). Adsorption of Cr (VI) ions onto goethite, activated carbon and their composite: kinetic and thermodynamic studies. *Applied Water Science*. 10(9): 1-18.

Adegoke, H. I., AmooAdekola, F., Fatoki, O. S., and Ximba, B. J. (2014). Adsorption of Cr (VI) on synthetic hematite (α-Fe2O3) nanoparticles of different morphologies. *Korean Journal of Chemical Engineering*. *31*(1), 142-154.

Ahalaya, N., Kanamadi, R.D. and Ramanchandra, T.V. (2005). Biosorption of chromium (VI) from aqueous solution by the husk of Bengal gram (*Ciera rientinum*). *Electron Journal of Biotechnology*. 8: 71–78.

Anamika, V.S., andBasant, K. Y. (2020). Adsorption study of Heavy Metals from Aqueous Solutions using Magnetite Nanoparticles.*Journal of Physics*. 1504:1-10.

Arunkumar, C., Perumal, R., and Lakshmi, N. (2014). Use of corn cob as low cost adsorbent for the removal of nickel (II) from aqueous solution. *International Journal of Advanced Biotechnology Research*.5: 325–330.

Baohong, H., Yang, J., Wang, J., Tian, B., Bi, J., Wang, N., Li, X., and Huang, N. (2019). Nanomaterials for the

Removal of Heavy Metals from Wastewater. *Nanomaterials*. 9(424): 1-39.

Dada, A.O., Olalekan, A.P., Olatunya, A.M. and DADA, O. (2010). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk.IOSR *Journal of Applied Chemistry.* 3 (1): 38-45.

Debnath, A., Deb, K., Chattopadhyay, K. K., andSaha, B. (2016). Methyl orange adsorption onto simple chemical route synthesized crystalline α-Fe2O3 nanoparticles: kinetic, equilibrium isotherm, and neural network modeling. *Desalination and Water Treatment*. 57(29): 13549-13560.

Etim, U. J., Umoren, S. A., andEduok, U. M. (2016). Coconut coir dust as a low-cost adsorbent for the removal of cationic dye from aqueous solution. *Journal of Saudi Chemical Society*. 20: S67-S76.

Horsfall Jnr, M., and Spiff, A. I. (2005). Effects of temperature on the sorption of Pb2+ and Cd^{2+} from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass. *Electronic Journal of Biotechnology*. 8(2): 43-50.

Jaiswal,A., Banerjee, S., Mani, R. andChattopadhyaya, M.C. (2013) Synthesis, characterization and application of goethite mineral as an adsorbent. *Journal of Environmental Chemical Engineering*. 1: 281–289.

Khorshidi, N., and Azadmehr, A. (2018). Characterisation and adsorption properties of oxalate-loaded hematite composite for Cd (II) and Pb (II) adsorption. *Equilibrium models, thermodynamic and kinetic studies*. 51 (13): 2122–2137.

Krishnan, K. A., and Anirudhan, T. S. (2003). Removal of cadmium (II) from aqueous solutions by steam activated sulphurised carbon prepared from sugar cane bagasse pith: Kinetics and equilibrium studies. *Water SA*. 29(2): 147-156.

Labied, R., Benturki, O., EddineHamitouche, A. Y. and Donnot, A. (2018). Adsorption of hexavalent chromium by activated carbon obtained from a waste lignocellulosic material (*Ziziphus jujuba* cores): Kinetic, equilibrium, and thermodynamic study. *Adsorption Science and Technology*, 36(3-4): 1066-1099.

Levankumar, L., Muthukumaran, V. andGobinath, M. B. (2009). Batch adsorption and kinetics of chromium (VI) removal from aqueous solutions by *Ocimum americanum* L. seed pods. *Journal of Hazardous Materials*. 161(2): 709-713.

Li, W., Liu, J., Qiu, Y., Li, C., Wang, W. and Yang, Y. (2019). Polyethylene glycol modified magnetic nanoparticles for removal of heavy metal ions from aqueous solutions. *Journal of Dispersion Science and Technology*.40(9): 1338-1344.

Liu, Q. X., Zhou, Y. R., Wang, M., Zhang, Q., Ji, T., Chen, T. Y., and Yu, D. C. (2019). Adsorption of methylene blue from aqueous solution onto viscose-based activated carbon fiber felts: Kinetics and equilibrium studies. *Adsorption Science and Technology*. 37(3-4): 312-332.

Mondal, N. K., and Chakraborty, S. (2020). Adsorption of Cr (VI) from aqueous solution on graphene oxide (GO) prepared from graphite: equilibrium, kinetic and thermodynamic studies. *Applied Water Science*. 10(2): 1-10.

Wang, Y., Peng, C., Padilla-Ortega, E., Robledo-Cabrera, A., and López-Valdivieso, A. (2020). Cr (VI) adsorption on activated carbon: mechanisms, modeling and limitations in water treatment. *Journal of Environmental Chemical Engineering*, 8(4): 104031.

Saha, P., and Chowdhury, S. (2011). Insight into adsorption thermodynamics. *Thermodynamics*. 16: 349-364.

Schwertmann, U. and Cornell, R. M., (2007). Iron Oxides in the laboratory, Preparation and characterization. *Wiley VCH Verlag GmbH, Weinheim, Germany.* doi:10.1002/9783527613229

Wang, Y., Zhang, N., Chen, D., Ma, D., Liu, G., Zou, X., Chen, Y., Shu, R., Song, Q. and Lv, W. (2019). Facile synthesis of acid-modifed UiO_6 to enhance the removal of Cr (VI) from aqueous solutions. *Sci Total Environ*. 682: 118–127.