

# Adsorption Isotherms and Thermodynamics Study of Cd (II), Cr (III) and Cr (VI) binding by Natural Goethite and Synthetic Goethite Adsorbents

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## ABSTRACT

*Batch adsorption studies of some heavy metal ions; Cd (II), Cr (III) and Cr (VI) ions were conducted on a natural goethite (NGT) and compared same with a synthetic goethite (SGT). The influence of NGT particle size, initial adsorbate concentration, initial solution pH, adsorbent dosage and temperature on the adsorption efficiency was investigated using batch equilibrium assays. The adsorption data was fitted into three common isotherm models; Langmuir, Freundlich and Temkin models. Thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  and isosteric heat of adsorption ( $\Delta H_r$ ) were estimated. Results of the investigation showed that, adsorption processes were dependent on the various equilibrium parameters investigated. The adsorption behavior was essentially the same, although, SGT performed more excellently than NGT. The result of isotherm modeling revealed the order of fittings; Langmuir > Temkin > Freundlich. The adsorption process was found to be feasible and spontaneous ( $\Delta G = -ve$ ). Also,  $\Delta H$  and  $\Delta S$  for the processes are shown thus; Cd (II) and Cr (III) ions ( $\Delta H = +ve$ ,  $\Delta S = -ve$ ) and Cr (VI) ion ( $\Delta H = +ve$ ,  $\Delta S = +ve$ ). Additionally, the best fitting isotherm model, magnitudes of  $\Delta H$  and  $\Delta H_r$  suggested a combined physisorption and chemisorptions mechanism. Therefore, combined results of the study could provide useful information on the adsorption characteristics of these heavy metal ions onto goethite surfaces.*

**Keywords:** Adsorption, Natural goethite, Synthetic goethite, Isotherm, Thermodynamics

## INTRODUCTION

Heavy metals were since identified as one of the major causes of environmental pollution<sup>1</sup>. Heavy metals are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment, leading to accumulation in living organisms, causing various diseases and disorders<sup>2</sup>. Water contamination by heavy metals is more pronounced than other pollutants exposed to the natural ecosystem. It is well known that some metals are harmful to life, such as

antimony, chromium, copper, lead, manganese, mercury, cadmium etc., and are significantly toxic to human beings and the ecological environments<sup>3</sup>.

There are several methods which can be used to treat wastewater. The technologies can be divided into three categories: biological, chemical and physical. Among those methods, adsorption is widely used for its maturity and simplicity<sup>4</sup>. Adsorption has been developed as an efficient method for the removal of heavy metals from contaminated water and soil. It is generally

acclaimed as a powerful technique for heavy and toxic ions remediation. The adsorption process has many advantages such as: low cost of adsorbent, easy availability, low operational cost, ease of operation compared to other processes, reuse of adsorbent after regeneration, capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex form of metals that is generally not possible by other methods, environmentally friendly, cost effective and technically feasible alternative due to utilization of biomaterials, utilization of industrial, biological and domestic waste as adsorbents<sup>5</sup>.

A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, micro-organisms, sewage sludge, fly ash and activated carbon have been used for heavy metals removal<sup>6</sup>. Iron is the fourth most abundant element in the earth's crust (5.1 mass %). Iron ore deposits have been found in various locations in Nigeria, but mainly in the north-central, north-east and south-east regions. Iron oxides, which are introduced into nature by weathering of rocks, are widely distributed in air, water and soil mostly as goethite,  $\alpha$ -FeOOH<sup>7</sup>. Rust, the end product of corrosion, consists of goethite, which also play important role in regulating the concentration/distribution

of nutrients and heavy metal based pollutants in plants. If prepared synthetically, Goethite has certain advantages over their naturally occurring counterparts because of their purity and tailor-made composition with desired particle size, surface properties and colour<sup>7</sup>. Synthetic goethite have been extensively studied and applied for the removal of heavy metal contaminants from industrial solutions, radio nuclides from nuclear reactor plants and for municipal water treatment<sup>8</sup>.

Currently, there is no system to connect the unregulated industries to the common effluent treatment plant if there is any, which is highly essential in poor countries like Nigeria that have limited water resources. The poor treatment of industrial effluents is due partly to high cost of maintaining effluent treatment plants and to poor enforcement of relevant laws. Efficient adsorbent and adsorption process will reduce the cost of maintaining efficient effluent treatment plants. Therefore, investigating the effectiveness of natural goethite (NGT) and synthetic goethite (SGT) in the adsorption of some heavy metal ions (Cd (II), Cr (III) and Cr (VI) ions) from aqueous solution became necessary. This study was equally carried out to provide one the insights into the

mechanisms and thermodynamics of metal ions adsorption on both goethite surfaces.

## MATERIALS AND METHODS

### *Preparation and Characterization of Adsorbents*

Samples of NGT and SGT used in this study were prepared and characterized according to standard procedures and methods, and the results published elsewhere by Abdus-Salam *et al.*<sup>9</sup>.

### *Adsorption Experiment*

Batch mode adsorption study for Cd (II), Cr (III) and Cr (VI) was carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage, pH, temperature and contact time on NGT and SGT. 15 ml of different concentrations; 5-400 ppm of Cd (II), 5-500 ppm of Cr (III) and 5-200 ppm of Cr (VI) ions were contacted with 0.5 g NGT (varying particle sizes; 0.112 mm, 0.25 mm and 0.50 mm) and 0.1g SGT in 100 ml capacity conical flask, and agitated on an orbital mechanical shaker for 2 hr. The solutions were filtered and the filtrates then analyzed for metal ions (Cd (II) and Cr (III) ions) by using atomic absorption Spectrophotometer (AAS), and for Cr (VI) ion using UV-Visible spectrophotometer at a predetermined wavelength of maximum absorption ( $\lambda_{\max}$ )<sup>10,11</sup>. The optimum

concentrations of the various adsorbates were then selected for use in subsequent experiments.

Further experiments were conducted using the optimum concentrations to examine the effects of initial solution pH (varied from 2 to 8), variation of adsorbent dose (varied from 0.05 to 0.50 g), agitation time (varied from 5 to 120 minutes) and temperature (varied from 303 to 333K).

The analyte ions adsorbed by the adsorbents at equilibrium were determined using a mass balance equation<sup>12</sup>.

$$q_e = \frac{(C_i - C_e)}{S} \quad (1)$$

Where  $q_e$  is the analyte ions concentration adsorbed on the adsorbent at equilibrium (mg/g),  $C_i$  is the initial concentration of analyte ions in the solution (mg/L) and  $C_e$  is the equilibrium concentration or final concentration of analyte ion in the solution (mg/L). The dose (slurry) concentration,  $S$  is expressed by equation 2:

$$S = \frac{m}{V} \quad (2)$$

Where  $v$  is the initial volume of analyte ions in solution (L) used and  $m$  is the mass of the adsorbent used (g).

## THEORY

### *Adsorption Isotherm Models*

In this study, three common isotherm models; Langmuir, Freundlich and Temkin models were tested for fitness of experimental data, and the linear forms of their equations presented in equations 3-5 respectively<sup>13,14,15</sup>.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$q_e = B \ln A + B \ln C_e \quad (5)$$

Where  $q_e$  is the adsorption capacity at equilibrium ( $\text{mg.g}^{-1}$ ),  $C_e$  is the equilibrium concentration of the adsorbate in  $\text{mg/L}$ ,  $K_a$  is a curve fitting parameter for equilibrium model and  $q_m$  is the maximum adsorption capacity,  $K_F$  and  $n$  are Freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively ( $\text{mgL}^{-1}$ ),  $A$  ( $\text{L/g}$ ) is Temkin isotherm constant and  $b$  ( $b = \frac{RT}{B}$ ,  $\text{J/mol}$ ) is a constant related to heat of sorption.

From the Langmuir equation, the favorable nature of adsorption can be expressed in terms of dimensionless separation factor,  $R_L$  of equilibrium parameter, which is defined by equation 6.

$$R_L = \frac{1}{1 + K_a C_0} \quad (6)$$

Where  $C_0$  is the initial concentration of the adsorbate in solution<sup>16</sup>.

### *Adsorption Thermodynamics*

In order to fully understand the nature of adsorption, thermodynamic parameters such as Gibb's free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ), and isosteric heat of adsorption ( $\Delta H_r$ ) were calculated. Common thermodynamic equations used are presented in equations 7-9<sup>17,18,19</sup>.

$$\Delta G = -RT \ln K_C \quad (7)$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = \Delta H - T \Delta S \quad (9)$$

Where  $R$  is the gas constant,  $T$  is the absolute temperature,  $K_C$  ( $K_C = \frac{C_s}{C_b}$ ) is the concentration equilibrium constant which is the adsorption coefficient obtained from Langmuir equation,  $C_s$  is the concentration of the metal ion on the surface of adsorbent at equilibrium, and  $C_b$  is the concentration of the metal ion in the bulk solution at equilibrium.

## RESULTS AND DISCUSSION

### *Effect of Initial Adsorbate Concentration*

The results of effect of variation of initial solution concentration on the adsorption of

Table 1: Data for quantity adsorbed as function of initial solution concentration for Cd (II), Cr (III) and Cr (VI) onto NGT and SGT

Ci (mg/L)	Cd (II)		Ci (mg/L)	Cr (III)		Ci (mg/L)	Cr (VI)	
	Quantity adsorbed			Quantity adsorbed			Quantity adsorbed	
	$q_e$ (mg/g)			$q_e$ (mg/g)			$q_e$ (mg/g)	
	NGT	SGT		NGT	SGT		NGT	SGT
6	0.177	0.897	5	0.125	0.733	5	0.149	0.524
18	0.439	2.669	25	0.75	3.748	25	0.599	3.514
36	0.775	5.369	50	1.4625	7.498	50	1.1	6.671
72	1.398	10.77	75	2.15	11.25	100	1.993	10.28
100	0.497	13.6	100	2.85	14.99	150	0.711	17.77
150	0.409	21.88	150	2.5	19.08	200	0.61	9.787
200	-	26.89	200	2.255	22.48			
250	-	37.5	250	-	19.3			
300	-	42.83	300	-	18.45			
350	-	51.57	350	-	16.93			
400	-	50.84	400	-	15.41			
450	-	49.21						

From Table 1, the amount of analyte adsorbed per 0.5 g NGT and 0.1 g SGT increased with the increasing of the initial solution concentrations up to 72 mg/L for Cd (II) on NGT, 350 mg/L for Cd (II) on SGT, 100 mg/L for Cr (III) on NGT, 200 mg/L for Cr (III) on SGT, 100 mg/L for Cr (VI) on NGT, and 150 mg/L for Cr (VI) on SGT, after which the adsorption falls. The decrease in adsorption after reaching maximum may be attributed to the saturation of the adsorption sites of both

adsorbents at higher concentrations. The SGT in spite of its small mass (0.1 g) sorbed more quantity of all adsorbates and at higher concentration compared to NGT of mass 0.5 g. This may be as a result of the NGT sample containing less amount of pure goethite and more impurities than SGT. Hence, saturation of the adsorption sites of SGT was shifted to higher concentration. Similar observation was reported by Abdus-Salam and Adekola<sup>10</sup>.

### Effect of Natural Goethite Particle Size

Figures 1 – 3 represent the uptake of Cd (II), Cr (III), and Cr (VI) ions by NGT of

three different particle sizes (0.112, 0.250 and 0.500) mm.

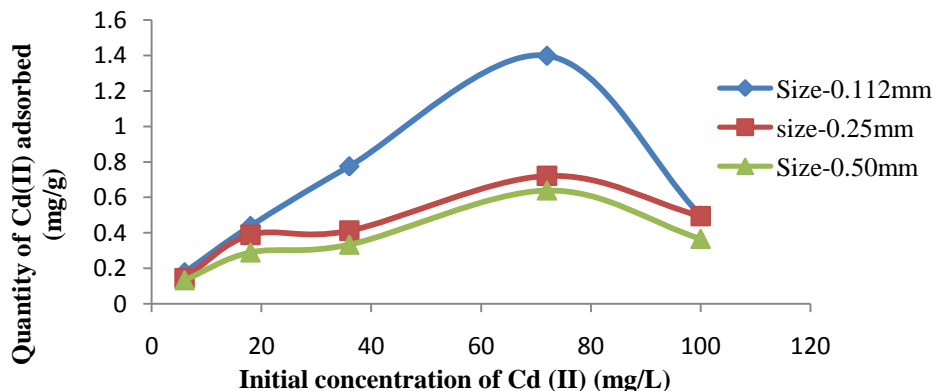


Figure 1: Effect of variation of particle size on Cd (II) adsorption at varying concentration

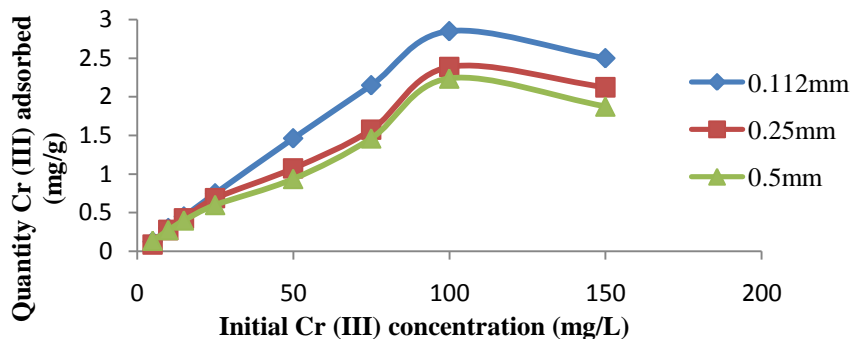


Figure 2: Effect of variation of particle size on Cr (III) adsorption at varying concentration

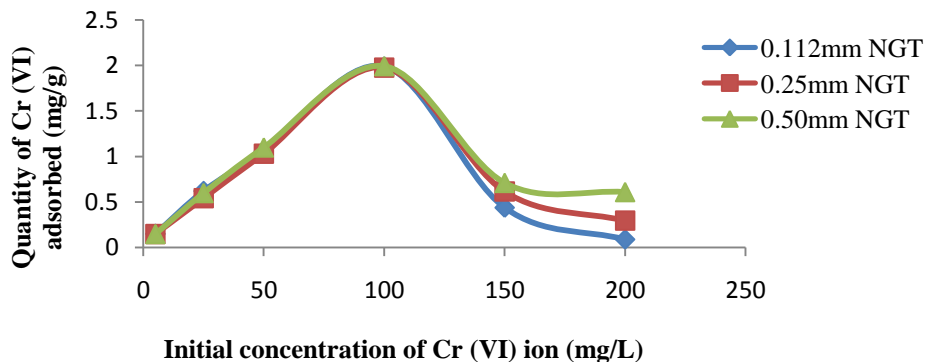


Figure 3: Effect of variation of particle size on Cr (VI) adsorption at varying concentration

From Figures 1 – 3, adsorption studies of metal ions by NGT indicated that sorption capacity is dependent on its particle size. The sample with particle size 0.112 mm exhibited the highest maximum adsorption efficiency for uptake of Cd (II) and Cr (III), and this may be attributed to the larger surface area provided by small particle size of the adsorbent material. Diffusional resistance to mass transport in the case of adsorbent with larger particle sizes is higher and most of the internal surface of these particles may not be accessible or utilized for adsorption. Consequently, the amount of Cd (II) and Cr (III) adsorbed were relatively less in

such cases. This observation is in agreement with the result obtained by Salami and Adekola<sup>20</sup>.

However, at maximum adsorption, there was no significant difference in the sorption of Cr (VI) by NGT of different particle sizes tested. As a result, in the succeeding experiments, NGT particle size of 0.112mm was utilized.

#### *Effect of Adsorbent Dosage*

Results of the adsorption experiments using six different dosages, 0.05, 1.0, 0.15, 0.20, 0.25 and 0.5 g, for both adsorbents at optimum concentrations of the various adsorbates were given in Figures 4 – 6.

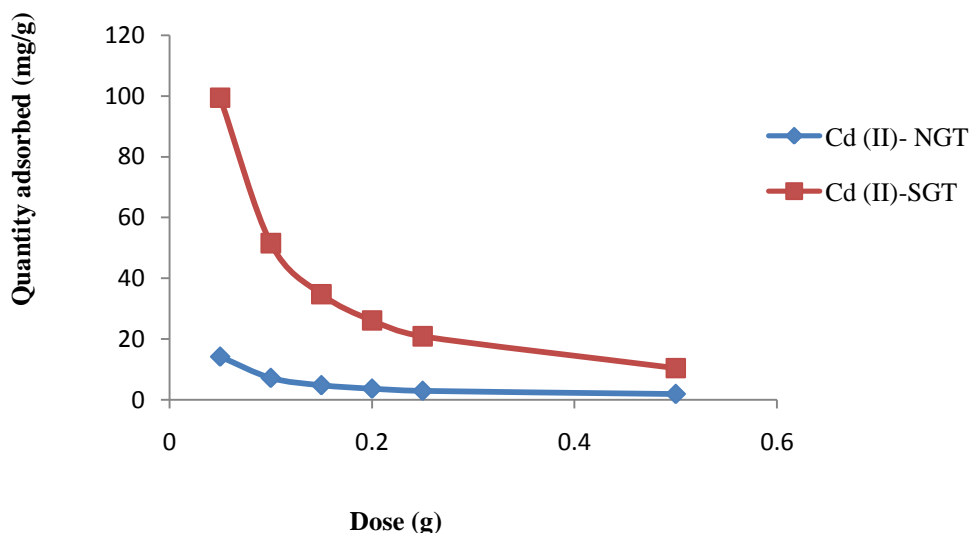


Figure 4: Effect of variation of adsorbent dosage on sorption of Cd (II) onto NGT and SGT

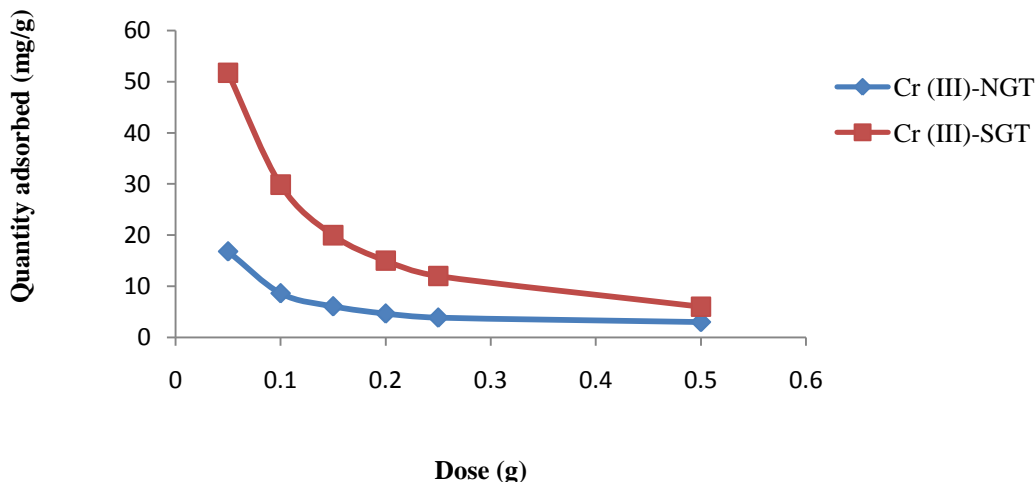


Figure 5: Effect of variation of adsorbent dosage on sorption of Cr (III) onto NGT and SGT

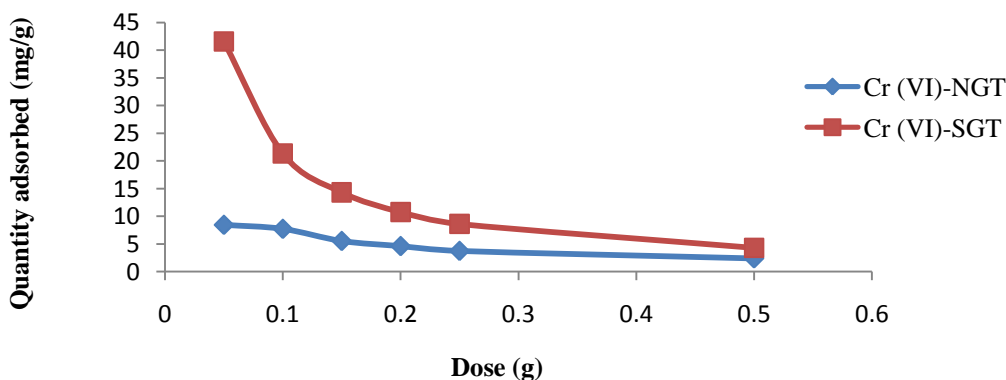


Figure 6: Effect of variation of adsorbent dosage on sorption of Cr (VI) onto NGT and SGT

The result of the effect of variation of adsorbent doses shown by the declining curves of  $q_e$  versus dose (Figure 4-6) indicated that, with increasing adsorbent load, the quantity of various adsorbates sorbed onto the unit weight of the adsorbents cuts down. This may be attributed to the overlapping or aggregation of adsorption sites, which leads to a decrease in total available

adsorbent surface area and an increase in diffusion path length. Similar result was reported by Crini and Badot<sup>19</sup>.

#### *Effect of Initial pH*

To observe the effect of pH on the extent of metal ions and dyes adsorption, solution pH was varied from 2 to 8. The quantities of metal ions removed at different pH were plotted in Table 2.



Table 2: Data for percent adsorbed/adsorption capacity as function of initial solution pH for Cd (II), Cr (III) and Cr (VI) onto NGT and SGT

Adsorbate	pH	NGT		SGT	
		% sorbed	qe (mg/g)	% sorbed	qe (mg/g)
Cd (II)	2	51.98	1.123	68.3	50.89
	3	52.27	1.129	82.28	51.07
	4	69.81	1.508	90.58	51.23
	5	80.45	1.738	95.24	51.35
	6	91.09	1.967	98.28	51.6
	7	93.42	1.769	99.47	45.05
	8	95.27	1.787	100	44.43
	Cr (III)	2	70.55	2.896	77.18
3		77.88	2.906	81.07	24.32
4		88.11	2.913	83.3	24.99
5		95	2.97	88.33	29.5
6		96.55	2.987	94.54	29.83
7		98.55	2.957	95.59	29.88
8		99.53	2.956	99.16	29.75
Cr (VI)		2	79.07	2.372	96.1
	3	72.07	2.162	42.24	9.504
	4	68.21	2.046	35.3	7.943
	5	67.93	2.038	30.6	6.885
	6	66.85	2.006	28.25	6.357
	7	66.48	1.994	12.51	2.816
	8	66.48	1.994	6.94	1.561

The results in Table 2 showed that there was a marked influence with a gradual rise in the uptake with increase in pH from 2 and reaching a maximum at pH of 6 for Cd (II)-NGT(1.123 mg/g to 1.967 mg/g), Cd (II)-SGT(50.89 mg/g to 51.6 m/g) and Cr

(III)-NGT(2.896 mg/g to 2.987 mg/g), and pH 7 for Cr (III)-SGT(23.15 mg/g to 29.88 mg/g) after which it falls gradually. The increase may be attributed to the fact that when pH of the solution was increased, an increase in the negative charge on the

goethite surface results, hence leading to increased adsorption of positively charged ions (Cd (II) and Cr (III)). A similar phenomenon in relation to the adsorption of certain cations on various adsorbents has been reported previously<sup>11,18,20</sup>. The observed fall in quantity adsorbed at pH above 6 for Cd (II) and Cr (III) onto NGT, and above 7 for Cr (III) onto SGT may be attributed to the precipitation of Cd (II) as Cd(OH)<sub>2</sub> and Cr (III) as Cr(OH)<sub>3</sub>. Similar observation had earlier been reported elsewhere<sup>10</sup>.

However, the adsorption of Cr (VI) ion onto both adsorbents showed opposite trend as their uptake increased with pH decrease. For an increase in Cr (VI) ion solution pH from 2 to 8, the quantity adsorbed decreased from 2.372 mg/g to 1.994 mg/g for Cr (VI)-NGT and 21.62 mg/g to 1.561 mg/g for Cr (VI)-SGT. This may be due to the fact that, in the acidic range of pH, chromium ions coexist in different forms such as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>4-</sup>, Cr<sub>3</sub>O<sub>10</sub><sup>2-</sup> and Cr<sub>4</sub>O<sub>13</sub><sup>2-</sup> amongst which HCrO<sub>4</sub><sup>-</sup> predominates. As the pH of the solution increases, the predominant species are then CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. More adsorption at acidic pH indicates that the lower pH results in an increase in H<sup>+</sup> ions on the adsorbent surface that result in significantly strong electrostatic attraction between positively charged adsorbent

surface and chromate ions. Lesser adsorption of Cr (VI) at pH values greater than 6.0 may be due to the dual competition of both the anions (CrO<sub>4</sub><sup>2-</sup> and OH<sup>-</sup>) to be adsorbed on the surface of the adsorbent, of which OH<sup>-</sup> predominates. This is in accordance with earlier studies that reported the removal of Cr (VI) by different adsorbents<sup>11,21</sup>.

For all experiment on the effect of initial solution pH on the sorption capacity of NGT and SGT, it is more realistic to note that, solution pH only have a slight effect on NGT when compared to SGT. Also the quantities of all adsorbates taken by SGT were relatively higher. Similar observation was been reported elsewhere by Abdusalam and Adekola<sup>10</sup>.

#### ***Adsorption Thermodynamics and Effect of Temperature***

In order to fully understand the nature of adsorption, thermodynamic parameters such as Gibb's free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and isosteric heat of adsorption ( $\Delta H_T$ ) were calculated from the data generated from the effect of temperature experiment. The results of thermodynamic parameters and effect of temperature plots for the adsorption of Cd (II), Cr (III) and Cr (VI) onto NGT and SGT are presented in Table 3.

Table 3: Thermodynamic parameters for the sorption of Cd (II), Cr (III) and Cr (VI) onto NGT and SGT

Adsorption Thermodynamics	Parameters					
	T (K)	q <sub>e</sub> (mg/g)	ΔG (kJ/mol)	ΔS (J/mol)	ΔH (kJ/mol)	ΔH <sub>r</sub> (kJ/mol)
Cd (II) - NGT	303	1.961	-5.77	67.28	14.71	-13.55
	308	1.967	-5.95	67.28	14.71	-13.55
	313	1.98	-6.24	67.28	14.71	-13.55
	318	1.999	-6.65	67.28	14.71	-13.55
	323	2.017	-7.11	67.28	14.71	-13.55
Cd (II) - SGT	303	51.41	-9.71	388.41	108.09	-107.35
	308	51.97	-11.75	388.41	108.09	-107.35
	313	52.19	-13.33	388.41	108.09	-107.35
	318	52.28	-14.5	388.41	108.09	-107.35
	323	52.44	-18.1	388.41	108.09	-107.35
Cr (III) - NGT	303	2.714	-5.67	288.39	82	-78.44
	308	2.796	-6.7	288.39	82	-78.44
	313	2.856	-7.77	288.39	82	-78.44
	318	2.929	-9.84	288.39	82	-78.44
	323	2.957	-11.33	288.39	82	-78.44
Cr (III) - SGT	303	28.63	-7.66	400.2	114.36	-112.54
	308	28.97	-8.56	400.2	114.36	-112.54
	313	29.46	-10.41	400.2	114.36	-112.54
	318	29.64	-11.69	400.2	114.36	-112.54
	323	29.93	-16.2	400.2	114.36	-112.54
Cr (VI) - NGT	303	2.35	-3.24	-102.65	-34.19	23.8
	308	2.16	-2.42	-102.65	-34.19	23.8
	313	2.05	-2	-102.65	-34.19	23.8
	318	1.92	-1.51	-102.65	-34.19	23.8
	323	1.81	-1.14	-102.65	-34.19	23.8
Cr (VI) - SGT	303	21.49	-7.69	-35.67	-16.82	15.89
	308	21.31	-7.4	-35.67	-16.82	15.89
	313	21.19	-7.25	-35.67	-16.82	15.89
	318	21.07	-7.12	-35.67	-16.82	15.89
	323	21	-7.08	-35.67	-16.82	15.89

As seen from Table3, the values of the Gibb's free energy change are all negative.

This indicated the feasibility and spontaneity of the adsorption process for the range of

temperatures tested. Similar result was reported by Ugbeet *al.*<sup>18</sup>, Muhammad *et al.*<sup>22</sup>, Ladanet *al.*<sup>11</sup> and Boparai *et al.*<sup>6</sup>. Also,  $\Delta G$  became increasingly negative with temperature for adsorption of Cd (II) and Cr (III) ions onto both adsorbents; an indicative of feasibility of the process at higher temperature (endothermic process). That is, quantity adsorbed increases with increase in solution temperature for Cd (II) and Cr (III) ions onto both adsorbents. The increased removal due to increasing temperature may be attributed to greater interaction between the reactive groups of the adsorbent and the adsorbates. More so, at higher temperatures there would be an increase in the mobility of the adsorbate ions thereby producing a swelling effect within the internal structure of the adsorbent, thus, enabling the metal ions to penetrate further. Similar trend was reported by Abdus-Salam and Buhari<sup>23</sup>, Landan *et al.*<sup>11</sup>, Chmielewska *et al.*<sup>24</sup> and Noshinet *al.*<sup>25</sup>. However, an opposite trend was observed for Cr (VI) ion on both adsorbents, as values of free energy change became decreasingly negative with temperature; an indication that adsorption is more favourable as solution temperature is lowered (exothermic process). That is, quantity adsorbed decreases with increase in solution temperature. This was attributed to the fact that at higher temperature, the physical interaction between the adsorbates and the adsorbent became

weaker due to weakening of hydrogen bonds and van der Waals interaction. Similar results were reported by Prabakaran and Arivoli<sup>26</sup>, Rattanaphaniet *al.*<sup>27</sup> and Chartterjee *et al.*<sup>28</sup>. The positive values of enthalpy change ( $\Delta H$ ) for adsorption of Cd (II) and Cr (III) ions showed that the process is endothermic; as evident in enhanced removal at increased temperature. Opposite trend was observed for adsorption of Cr (VI) ion on both adsorbents, as values of enthalpy change were negative; an indicative of exothermic process<sup>29</sup>. The magnitude of  $\Delta H$  falls into the range of 80–200 kJ mol<sup>-1</sup> for adsorption of Cd (II)-SGT, Cr (III)-NGT and Cr (III)-SGT, an indication that binding of these metal ions follows chemisorption mechanism. The adsorption of Cr (VI) ion on NGT fell between 20.9–80 kJ/mol; an indicative of combined mechanism of physisorption and chemisorptions at work. Adsorption of Cd (II)-NGT and Cr (VI)-SGT had enthalpy change below 20.9 kJ/mol, which indicated physical adsorption<sup>18,22,29</sup>. Positive value of the entropy change ( $\Delta S$ ) showed greater affinity of the adsorbent towards the adsorbate<sup>22</sup>. This is the case for Cd (II) and Cr (III) ions on both adsorbents. In addition, it showed increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate, gain more

translational entropy than is lost by the adsorbate, thus allowing for the prevalence of randomness in the system<sup>29</sup>. Opposite trend was observed for Cr (VI) ion on both adsorbent, where entropy change is negative, indicating low affinity for these adsorbates. The values of the isosteric heat of adsorption are > 40 kJ/mol for Cd (II)-SGT, Cr (III)-NGT, and Cr (III)-SGT, illustrating a chemisorption mechanism also taking part in the process (Muhammad *et al.*, 2014). For adsorption of Cd (II)-NGT, Cr (VI)-NGT, and Cr (VI)-SGT, values of isosteric heat of adsorption were < 40 kJ/mol, indicating that some element of physical adsorption was greatly involved in the adsorption process

<sup>18,22,29</sup>. On the basis of thermodynamic studies of the adsorption of Cd (II) on NGT, Cr (III) and Cr (VI) on NGT and SGT, the process was feasible, spontaneous and proceeded by a combined physisorption and chemisorptions mechanism as suggested by values of Gibb's free energy change, entropy change, the magnitudes of enthalpy change and isosteric heat of adsorption.

#### **Adsorption Isotherm**

The data obtained from the adsorption experiment were tested for fitness into three common adsorption equations; Langmuir, Freundlich and Temkin isotherms. The data generated for linearized isotherm parameters are presented in Table 4.

Table 4: Isotherm parameters for sorption of Cd (II), Cr (III) and Cr (VI) ions onto NGT and SGT

Isotherm Parameters	NGT			SGT		
	Cd (II)	Cr (III)	Cr (VI)	Cd (II)	Cr (III)	Cr (VI)
<b>Langmuir</b>						
$R^2$	0.01					
	1	0.9456	0.9812	0.9522	0.9903	0.9401
$K_L$ (L/g)	0.50					
	3	0.278	0.138	0.184	0.237	0.097
$q_{exp}$ (mg/g)	1.39					
	8	2.85	1.993	13.6	22.48	17.77
$q_m$ (mg/g)	4.45					
	2	2.648	0.617	31.022	16.287	16.309
$R_L$	0.02					
	69	0.0234	0.0676	0.0153	0.0207	0.0643
<b>Freundlich</b>						
$R^2$	0.59					
	48	0.4834	0.546	0.4708	0.2905	0.3014
$K_F$	0.35					
	8	0.658	0.409	13.008	9.499	2.75
$n$	4.45					
	2	2.217	4.936	3.34	8.718	3.435

Temkin $R^2$	0.8924	0.6775	0.2125	0.4185	0.5397 1.67E+0	0.1551 179.70
A (L/mg)	0.267	7.915	983.43	261.01	5	3
B (J/mol)	0.577	0.503 5008.2	0.0927 27175.	4.221	1.0705	1.081 2330.3
$b_0$ (J/mol)	4365.93	3	2	596.812	2353.24	8

The various values of regression coefficient,  $R^2$  (Table 4) indicated that the Langmuir isotherm model fitted best the adsorption processes except for adsorption of Cd (II) ion onto NGT where the  $R^2$  value (0.011) is far below unity. This is a deviation from most results obtained in literature for adsorption of Cd (II) ion on goethites and may be attributed to the surface characteristics and chemical composition of the goethite obtained from natural deposit (NGT). The goodness of fit of Langmuir isotherm indicated that adsorption of Cr (III) and Cr (VI) ions onto both adsorbents may follow monolayer coverage, uniform energies of adsorption onto the surface and no transmigration of the various adsorbates in the plane of the surface. Similar observation was reported by Abdus-Salam and Adekola<sup>10</sup>, Boparai *et al.*<sup>6</sup>.

Data generated from the adsorption experiment were subjected to the equation of separation factor,  $R_L$  in order to ascertain the favourability of the sorption process<sup>16</sup>. For a favourable adsorption,  $0 < R_L < 1$ , while for an unfavourable adsorption,  $R_L > 1$  and when  $R_L = 0$ , adsorption is linear and irreversible

process<sup>30</sup>. The separation factor,  $R_L$  values obtained from these adsorption processes showed favourability of the adsorption, i.e.  $0 < R_L < 1$ .

To further confirm the applicability of this model to the best fitting sorption systems, a comparison between values of maximum adsorption capacity,  $q_{max}$  and the experimentally determined  $q_e$  were equally reported in Table 4, which showed fair closeness of the two parameters ( $q_{max}$  and  $q_e$ ) for Cr(III) on NGT and Cr (VI) on SGT. The wide gap between  $q_e$  and  $q_{max}$  for most adsorption systems suggest that the adsorbate have no unrestricted access to the active sites, the binding energies are not the same and adsorption may not be monolayer even though the  $R^2$  values are encouraging.

The values of the regression coefficient,  $R^2$  (Table 4) obtained from the Freundlich isotherm modeling were fair for the heavy metals on NGT compared to those of their adsorption onto SGT. On the basis of this, it may be suggested that the adsorption of the heavy metals onto NGT proceeded by multilayer adsorption on already chemisorbed

layer. This is in agreement with results obtained by Boparai *et al.*<sup>6</sup>, Shahryariet *al.*<sup>16</sup>, and Abdus-Salam and Itiola<sup>30</sup>. The values of the Freundlich exponent,  $n$  were all above unity, indicating a high affinity between adsorbate and adsorbent and indicative of chemisorptions<sup>31,32</sup>. The data fitted fairly well into the Temkin isotherm model with  $R^2$  value of 0.8924 (Table 4) for adsorption of Cd (II) onto NGT. The Temkin adsorption equilibrium binding energy constant,  $A$  which relates to the adsorptive potential of an adsorbents were in the order: Cr (III)-SGT (1.67E+05 L/mg) > Cr (VI)-NGT (983.43 L/mg) > Cd (II)-SGT (261.01 L/mg) > Cr (VI)-SGT (179.703 L/mg) > Cr (III)-NGT (7.915 L/mg) > Cd (II)-NGT (0.267 L/mg). This showed that SGT has a greater adsorption potential on Cr (III) and Cd (II) than NGT, and on the other hand, NGT

possess a greater adsorption potential on Cr (VI) than SGT. The Temkin constant ( $b_0$ ) related to the heat of adsorption which decreases linearly rather than logarithmically as the surface of the adsorbent is loaded due to adsorbent-adsorbate interaction were given in the order: Cr (VI)-NGT (27175.2 J/mol) > Cr (III)-NGT (5008.23 J/mol) > Cd (II)-NGT (4365.93 J/mol) > Cr (III)-SGT (2353.24 J/mol) > Cr (VI)-SGT (2330.38 J/mol) > Cd (II)-SGT (596.812 J/mol), with SGT having the lower values. The lower values suggest that there is a greater interaction between the adsorbents and the adsorbates which corresponds to decrease in the heat of sorption of all molecules in the layer<sup>33</sup>. A Comparison of Temkin isotherm constants,  $b_0$  obtained in the present study with those of previous researches is presented in Table 5.

Table 5: Comparison of Temkin isotherm constant,  $b_0$  with those of previous researches

Adsorbent	Adsorbate	$b_0$ (J/mol)	Author
Agbani clay	Cd (II)	10540.34	34
NGT	Cd (II)	4365.93	Present study
SGT	Cd (II)	596.812	Present study
Diatomaceous earth	Cr (III)	1362.43	35
NGT	Cr (III)	5008.23	Present study
SGT	Cr (III)	2353.24	Present study
Diatomaceous earth	Cr (VI)	2113.37	35
NGT	Cr (VI)	27175.2	Present study
SGT	Cr (VI)	2330.38	Present study
<i>Saccharomyces cerevisiae</i>	EY	35.4	36

NGT	EY	9170.5	Present study
SGT	EY	702.89	Present study
Coconut coir dust	MB	568.66	37
Hulls of <i>vitexdoniana</i>	MB	89.87	38
NGT	MB	8777.5	Present study
SGT	MB	523.62	Present study

## CONCLUSION

In this study, the sorption of Cd (II), Cr (III), and Cr (VI) ions onto natural goethite (NGT) and synthetic goethite (SGT) was investigated in order to ascertain the effectiveness of both adsorbents. From the adsorption data, the sorptive property of the natural and synthetic goethite was found to be dependent on initial adsorbate concentration, initial solution pH, adsorbent dosage, and temperature. Also, the variation of NGT particle sizes had influence on the adsorption capacity. Both adsorbent showed similarities in trend for the various metal ions, with SGT performing excellently. The higher adsorption capacity of SGT was attributed to the relatively higher proportion of goethite in SGT per unit mass of sample used, rather than its greater chemical reactivity. Consequently, NGT cannot compete favourably with SGT for

decontamination of the heavy metals from aqueous waste.

Additionally, the isotherm modeling revealed the order of fittings: Langmuir > Temkin > Freundlich. The favorable and spontaneous adsorption of these metal ions was signified by the obtained values of the separation factor,  $R_L$  and the Gibbs free energy change,  $\Delta G$ . Furthermore, the adsorption process was found to be exothermic for Cr (VI) ion and endothermic for Cd (II) and Cr (III) ions. Also, the adsorption proceeded by a combined physisorption and chemisorptions mechanism as suggested by the magnitudes of enthalpy change ( $\Delta H$ ), isosteric heat of adsorption ( $\Delta H_r$ ) and best fitting isotherm model.

Finally, this study could provide useful information on metal ion fixation onto goethite surfaces.



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