

Adsorptive removal of Cd^{2+} , Cr^{3+} and Cr^{6+} using natural and synthetic goethite particles: Kinetics study

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Abstract

The adsorption study of Cd^{2+} , Cr^{3+} and Cr^{6+} on natural goethite (NGT) and synthetic goethite (SGT) particles was conducted using batch equilibrium assays to investigate the influence of agitation time on the adsorption process. The data generated were thereafter fitted into six common kinetics models; pseudo-first order, pseudo-second order, Elovich, second order, intra-particle diffusion and film diffusion models. Results showed a rapid uptake and reached equilibrium at 60 minutes for Cr^{3+} -SGT ($q_e = 29.84$ mg/g), 90 minutes for Cd^{2+} -NGT (1.877 mg/g), Cd^{2+} -SGT (51.57 mg/g), Cr^{3+} -NGT (2.92 mg/g) and Cr^{6+} -NGT (2.372 mg/g), and 120 minutes for Cr^{6+} -SGT (19.035 mg/g). The adsorption kinetics revealed the order of fittings: Pseudo-second order > Elovich > Second order > Pseudo-first order, as well as intra-particle diffusion > film diffusion. Additionally, combined results of the kinetic modeling suggested that adsorption of the metal ions onto both adsorbents followed chemisorption process and that the mechanism of the adsorption occurred either by a combination of intra-particle and film diffusion, or that other processes occurred simultaneously with these two processes. The result of this study therefore, could provide useful information on the sorption of these heavy metal ions on both goethite forms.

Keywords: Adsorption; Kinetics; Natural goethite; Synthetic goethite; Heavy metal ions

1. Introduction

The continuous industrialization and rapid global development has yielded in the release of objectionable pollutants into the environment [1]. Amongst them the introduction of heavy metals through both natural and human activities has severe negative impact on the environment and has adverse effects on both aquatic and human life [2]. It is also responsible for the pollution of rivers and springs [3].

Several industries such as electroplating, battery manufacturing, paper, painting, pigments, fuels, photographic materials and metalworking etc. discharge heavy metals, including chromium (Cr) and cadmium (Cd) ions in large amounts in their effluents [4]. This has become worrisome and constitutes a matter of global concern in recent decades because their presence in non-permissible concentration in the environment poses a great hazard to human life [5]

Many techniques have been developed and applied to overcome the problems of treatment of toxic metals discharge including biological, air flotation and chemical treatments [6] such as catalytic and photocatalytic oxidation methods, chemical precipitation and adsorption on different media as adsorbents varying from synthetic materials [7] to agricultural products [8], [9]. Adsorption is one of the most popular methods amongst these,

especially using waste materials as the adsorbent(s) because of their low cost, high efficiency and ease of handling [10], [11].

Sorption of heavy metal ions using activated carbon adsorbent is a popular method but with little use in developing countries as a result of high cost of the adsorbent. In search of low-cost adsorbents, some researchers investigated the adsorption properties of locally available materials such as mango seed [12], orange peels [13], [14], Maize cob [15], rice husk [16], date palm seed [17], [18], [19], termite mound [20] amongst others.

Iron ore deposits are found in many locations in Nigeria, but majorly in the north-central, north-east and south-east regions [21]. Iron oxides, which are introduced into nature by weathering of rocks, are widely distributed in air, water and soil mostly as goethite [22]. Goethite ($\text{FeO}(\text{OH})$ or $\alpha\text{-FeOOH}$), is an iron mineral bearing hydroxy group which enables it to bind strongly to both organic and inorganic ligands [23]. Goethite particles show high specific surface areas and strong affinities for surface binding of oxyanions and heavy metals [24], thereby making it a choice of adsorbent in this study. Synthesized goethite when compared with their naturally occurring counterparts has an improved purity and tailored composition with desired particle size, surface properties and colour [22].

Many researchers have extensively studied and applied goethite particles (both natural and synthetic forms) for the adsorption of heavy metal contaminants from industrial

wastewater and for township water treatment [25], [26], [27], [28], [29].

This research therefore is aimed at investigating the kinetics of adsorption of toxic metal ions; Cd²⁺, Cr³⁺ and Cr⁶⁺ onto natural goethite (NGT) and synthetic goethite (SGT) surfaces with the objective of suggesting plausible mechanism of binding.

2. Materials and methods

2.1. Preparation and characterization of adsorbents

Sample of NGT of high grade quality was collected from the National Iron Ore Mining Company (NIOMCO), Itakpe, Kogi State, Nigeria. SGT (α -FeOOH) particles were synthesized in the laboratory according to the method reported by [30]. Both Samples were then prepared and characterized using the following instrumental methods: X-ray fluorescence (XRF) for elemental compositions of the adsorbents, Fourier Transform Infrared Spectrometry (FTIR) for surface functional groups, and Scanning Electron Microscopy (SEM) for grain size and morphological properties. An experiment to determine the point of zero charge was also conducted on both adsorbents. The results of the various investigations were however published separately by Abdus-Salam *et al* [31].

2.2 Adsorption experiment

Batch mode adsorption study was carried out to investigate the effect of agitation time on the sorption of Cd²⁺, Cr³⁺ and Cr⁶⁺ ions onto NGT and SGT. 15 ml solution each of Cd²⁺, Cr³⁺ and Cr⁶⁺ ions at their various optimum working concentrations as obtained from the results of variation of initial solution concentration earlier published by Ugbe *et al* [26] (72 mg/L for Cd²⁺-NGT, 350 mg/L Cd²⁺-SGT, 100 mg/L Cr³⁺-NGT, 200 mg/L Cr³⁺-SGT, 100 mg/L Cr⁶⁺-NGT and 150 mg/L for Cr⁶⁺-SGT) were contacted with both adsorbents (0.5 g NGT of particle size 0.112 mm and 0.1g SGT) in 100 ml capacity conical flask, and agitated on an orbital mechanical shaker at varying times (5 to 120 minutes). Each solution was then filtered and the filtrates analyzed for metal ions (Cd²⁺ and Cr³⁺) by using atomic absorption Spectrophotometer (AAS), and for Cr⁶⁺ ion using UV-Visible spectrophotometer at a predetermined wavelength of maximum absorption (λ_{max}) [25], [32].

The analyte ions adsorbed by the adsorbents at equilibrium were determined using the mass balance equation (eqn 1) [33].

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

Where q_e is the analyte ions concentration adsorbed on the adsorbent at equilibrium (mg/g), v is the initial volume of analyte ions in solution (L), C_i and C_e is the initial concentration and equilibrium concentration of analyte ions in the solution (mg/L) respectively, and m is the mass of the adsorbent used (g).

2.3. Theory

The kinetic study is necessary for an adsorption process because it depicts the uptake rate of the adsorbate towards the adsorbent and controls the remaining time of the whole adsorption process [34]. The kinetic study has the important practical task to determine the degree of utilization of the adsorption capacity as a function of the time of contact between the liquid and the solid in adsorption process. In the present study, six models were being treated; Pseudo first order, Pseudo second order, Second order, Elovich, intraparticle diffusion, and film diffusion models.

Pseudo first order is the earliest model used to describe adsorption rate pertaining to adsorption capacity [35] with the linear equation stated thus [36].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min) respectively, k_1 (min^{-1}) is the pseudo first order rate constant. The values of k_1 and q_e can be obtained from the slope and intercept respectively of the linear plot of $\ln(q_e - q)$ against t .

On the other hand, pseudo second order model is based on the assumption that the rate-limiting step may be chemical sorption (chemisorption) involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate. In addition, it is assumed that the sorption capacity is proportional to the number of active sites occupied on the adsorbent [37], [38] with the equation stated thus:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (3)$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min) respectively, and k_2 (g/mg/min) is the pseudo second order rate constant. The values of q_e and k_2 can be obtained from the slope and intercept respectively of the linear plot of t/q against t .

Second order model corroborates the chemisorption process of adsorption [39], likewise the Elovich model. Elovich model is unique in describing the heterogeneity of the adsorbent surface and that the rate of adsorption decreases exponentially (with time) with the amount of solute adsorbed due to increase coverage on the surface of the adsorbents [40]. The Elovich and Second order rate equations are presented in eqn 4 and 5 respectively.

$$q_t = \alpha \ln(a \alpha) + \alpha \ln t \quad (4)$$

Where q_t represents the amount of analyte adsorbed at time t , a , the desorption constant, and α , initial adsorption rate. The values of α and a can be obtained from the slope and intercept respectively of the linear plot of q_t versus $\ln t$ [37].

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_e} \quad (5)$$

Where C_e and C (mg/L) is the concentration of solute at equilibrium and at time t (min) respectively, and k_2 (L/(mg·min)) is the rate constant. k_2 can be obtained from the slope of the linear plot of $1/C_t$ vs t .

There are several steps involved in the adsorption of adsorbate by an adsorbent. These steps (which can be the rate controlling steps) involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates (film diffusion) and diffusion of the solute molecules into the interior of the pores (intraparticle diffusion), which is usually a slow process, these steps are being referred to as the mechanism of adsorption and cannot be explained by the kinetics of chemical reactions [41], [42]. In order to establish the rate controlling step of the uptake of these metal ions on the goethite particles, intraparticle diffusion equation also known as Weber–Morris equation was used as stated thus:

$$q_t = k_i t^{1/2} + C \quad (6)$$

Where K_{id} (mg/g/min^{1/2}) is the intraparticle diffusion rate constant or coefficient, and can be obtained from the slope of the linear plot of q_t against $t^{1/2}$. C is the intercept; the boundary layer thickness is described by the values of the intercept. The larger the intercept, the greater is the boundary layer effect [41].

Film diffusion on the other hand is given by:

$$\ln \left[1 - \frac{q_t}{q_e} \right] = -R^1 t \quad (7)$$

Where R^1 (min⁻¹) is liquid film diffusion constant and can be obtained by the linear plot of $\ln [1 - q_t/q_e]$ against t . q_t and q_e are the quantities adsorbed at time t and at equilibrium respectively [42], [43].

3. Results and discussion

3.1. Characterization

Results of the characterization of NGT and SGT as adapted from Abdus-Salam *et al* [31] are presented in Table 1 and Figures 1 to 3.

Table1: The elemental composition of NGT and SGT by XRF

Element	Intensity	Content (%)	Element	Intensity	Content (%)
NGT			SGT		
P	0.0004	0.0151	Mg	0.0000	0.0182
Ca	0.0077	0.1346	P	0.0002	0.0032
V	0.0004	0.0204	Ca	0.0058	0.0902
Cr	0.0009	0.0556	V	0.0004	0.0210
Mn	0.0014	0.0946	Cr	0.0010	0.0619
Co	0.0059	0.4262	Mn	0.0012	0.0823
Fe	0.6960	66.1930	Co	0.0056	0.4024
Ni	0.0010	0.0572	Fe	0.6982	66.4009
Cu	0.0010	0.0205	Ni	0.0012	0.0724
Zn	0.0010	0.0320	Cu	0.0009	0.0196
Pb	0.0060	0.1927	Zn	0.0011	0.0361
Sn	0.0008	0.1238	Pb	0.0067	0.2151
Sb	0.0007	0.0764	Rb	0.0023	0.0077
Rb	0.0019	0.0066	Mo	0.0007	0.0849
			Sn	0.0007	0.1202
			Sb	0.0006	0.0672

(Adapted from Abdus-Salam *et al* [31])

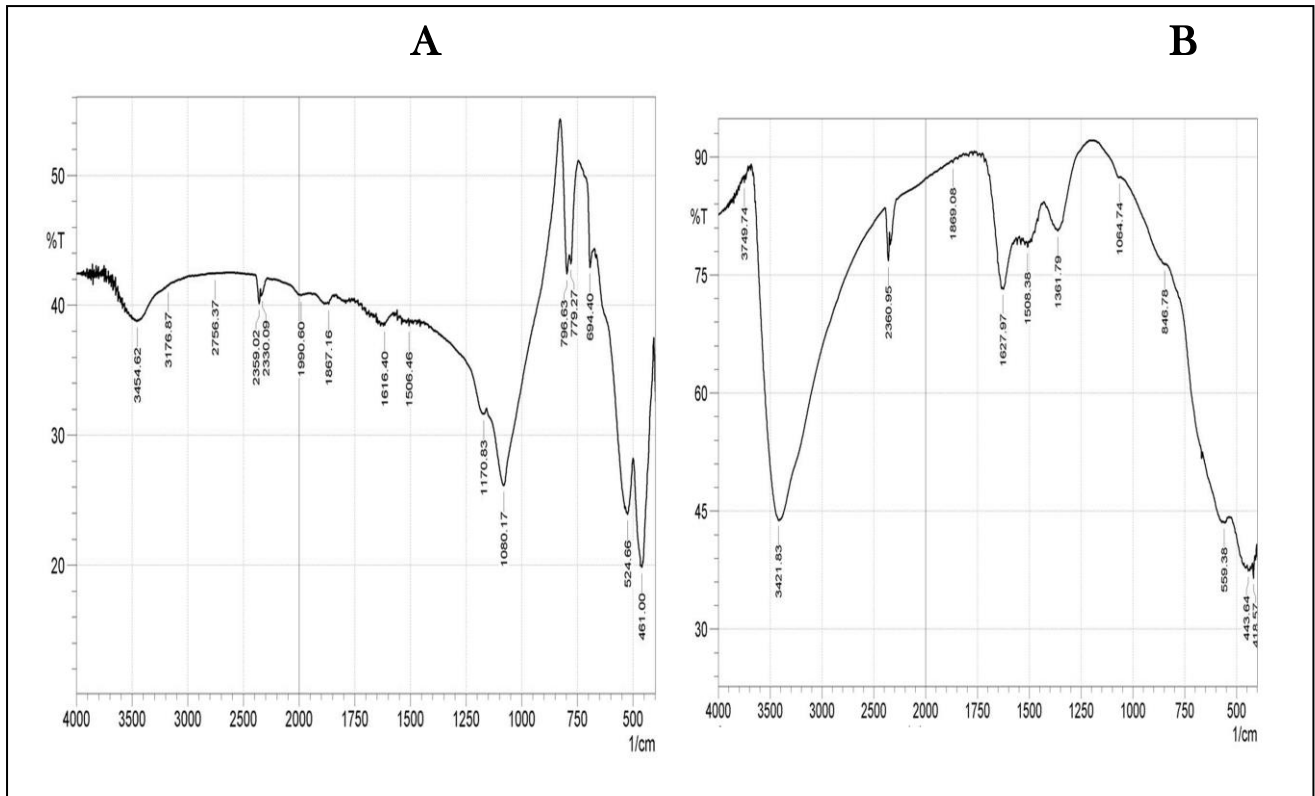


Figure 1. (A) IR spectrum of NGT, (B) IR spectrum of SGT (Adapted from Abdus-Salam *et al.* [31])

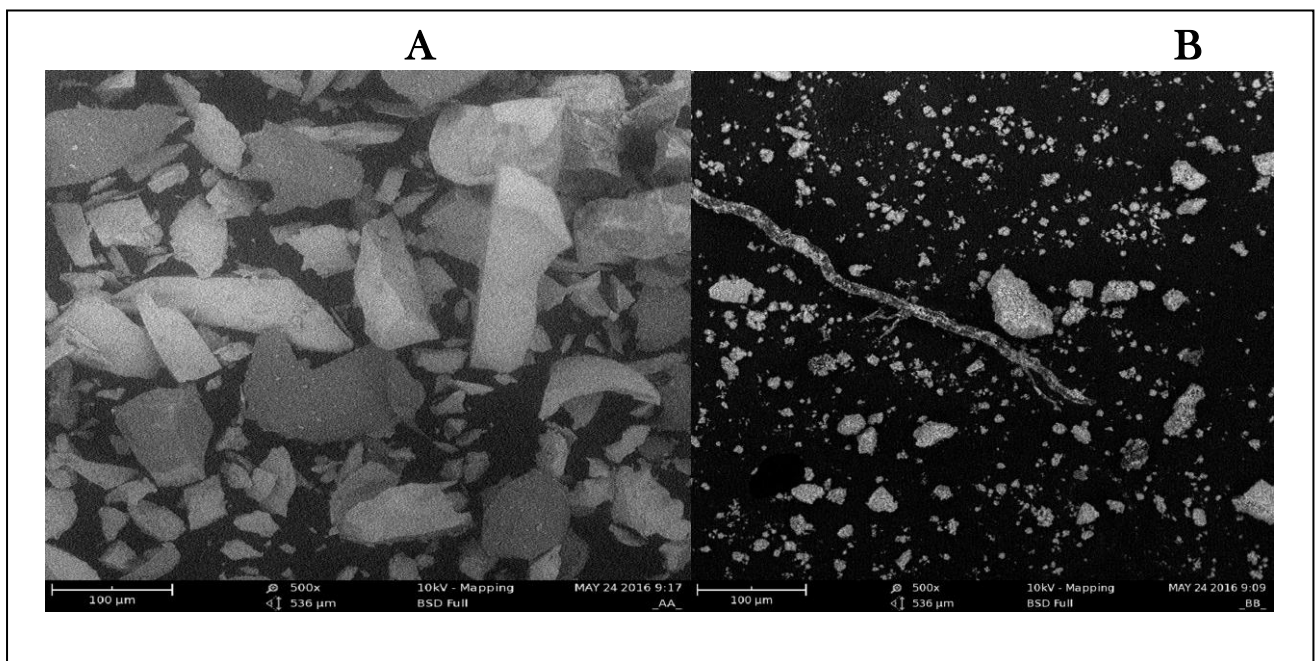


Figure 2. (A) SEM micrograph of NGT, (B). SEM micrograph of SGT (Adapted from Abdus-Salam *et al.* [31])

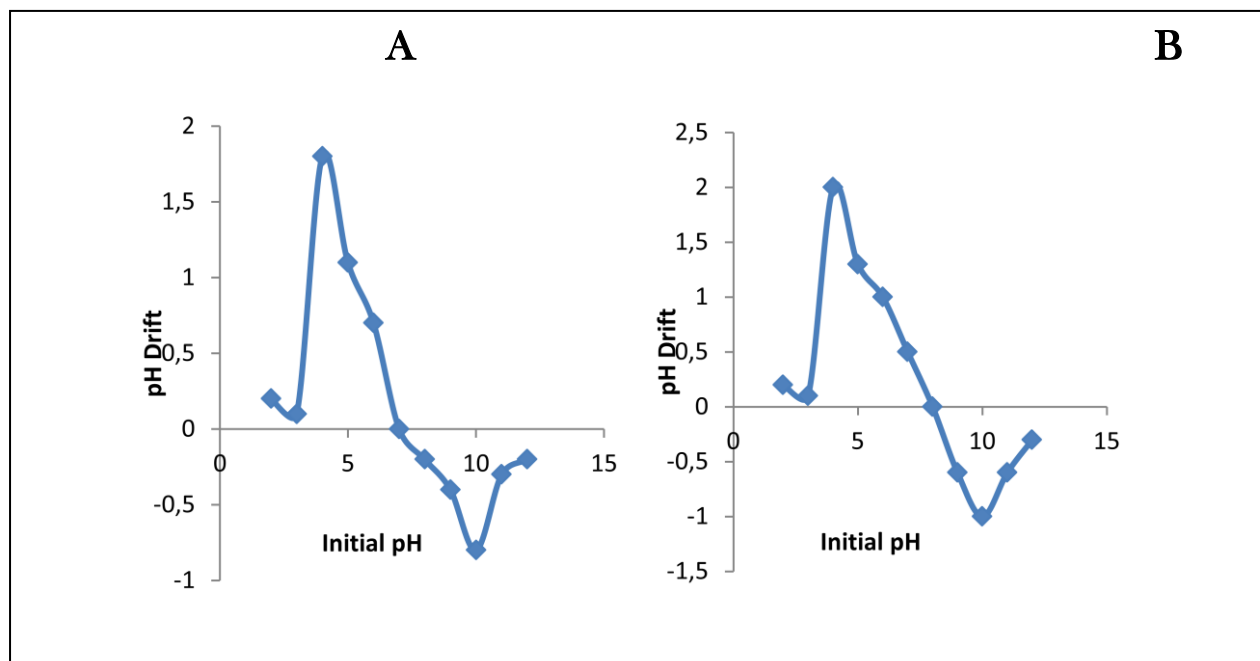


Figure 3. (A) Point of zero charge curve for NGT, (B) Point of zero charge curve for SGT (Adapted from Abdus-Salam *et al.* [31])

The combined results of characterization of both adsorbents showed their suitability for the sorption of heavy metal contaminants [31].

different time duration (5 to 120 minutes) at constant initial concentration of the various adsorbates, and the results illustrated in Table 2.

3.2. Effect of agitation time

The effects of agitation time on the adsorption of Cd²⁺, Cr³⁺ and Cr⁶⁺ ions onto NGT and SGT were studied at

Table 2: Effect of agitation time on the adsorption of Cd²⁺, Cr³⁺ and Cr⁶⁺ onto NGT and SGT

t (mins)	Quantity adsorbed, q _t (mg/g)					
	Cd ²⁺ -NGT	Cd ²⁺ -SGT	Cr ³⁺ -NGT	Cr ³⁺ -SGT	Cr ⁶⁺ -NGT	Cr ⁶⁺ -SGT
5	0.844	41.63	2.599	25.99	2.318	3.098
10	0.983	48.56	2.776	26.99	2.336	17.07
15	1.083	50.05	2.793	27.66	2.341	17.28
25	1.089	50.48	2.809	28.16	2.345	17.47
45	1.142	50.64	2.813	28.5	2.333	17.75
60	1.268	50.7	2.846	29.84	2.326	18
90	1.877	51.57	2.92	29.83	2.372	18.87
120	1.493	51.32	2.918	29.78	2.367	19.04

Table 2 showed fast uptake by these adsorbents as agitation time was increased from 5 minutes and reached equilibrium at 60 minutes for Cr³⁺-SGT (29.84 mg/g), 90 minutes for Cd²⁺-NGT (1.877 mg/g), Cd²⁺-SGT (51.57 mg/g), Cr³⁺-NGT (2.92 mg/g) and Cr⁶⁺-NGT (2.372 mg/g), and 120 minutes for Cr⁶⁺-SGT (19.035 mg/g). The adsorption of the various metal ions were generally characterized by a rapid adsorption within the first 5 min of agitation, which was followed by only a slight increase in uptake until equilibrium was attained, after which it was later slowed down with minimal incremental adsorption, although the quantities of all adsorbates taken by SGT were relatively higher. This is the general characteristic of adsorption of various adsorbates on iron oxides [25], [44].

Generally, the adsorption took place at the more reactive surface sites; as these sites were progressively filled, the more difficult the sorption becomes, as the sorption experiment tends to be more unfavourable. This was as a result of saturation of adsorption sites of adsorbent at higher contact time [45].

3.3. Adsorption kinetics

The data generated from the effect of agitation time experiment were fitted into six kinetic models; Pseudo first order, Pseudo second order, Second order, Elovich, intraparticle diffusion, and film diffusion models. The parameters obtained from the various plots are presented in Tables 3 - 5.

Table 3: The Pseudo-first order and pseudo-second order parameters for Cd²⁺, Cr³⁺ and Cr⁶⁺ on NGT and SGT

Adsorption Kinetics	Pseudo-first order			Pseudo-second order		
	k ₁ (min ⁻¹)	q _e (mg/g)	R ²	k ₂ (g/mg/min)	q _e (mg/g)	R ²
Cd ²⁺ - NGT	0.0597	2	0.2063	0.057	1.69	0.9466
Cd ²⁺ - SGT	0.0212	3.553	0.6755	0.024	51.81	0.9999
Cr ³⁺ - NGT	0.0776	0.548	0.4818	0.336	2.935	0.9998
Cr ³⁺ - SGT	0.0643	1.944	0.2467	0.025	30.12	0.9998
Cr ⁶⁺ - NGT	0.0016	0.036	0.019	1.313	2.369	0.9999
Cr ⁶⁺ - SGT	0.099	34.28	0.7326	4.36E-03	21.19	0.96

Table 4: The Second order and Elovich model parameters of Cd²⁺, Cr³⁺ and Cr⁶⁺ on NGT and SGT

Adsorption Kinetics	Second Order			Elovich		
	k ₂	C ₀ (mg/L)	R ²	a	α	R ²
Cd ²⁺ - NGT	0.0004	49.26	0.399	19.114	0.2478	0.7137
Cd ²⁺ - SGT	0.001	29.85	0.7872	1.56E+07	2.3726	0.6595
Cr ³⁺ - NGT	0.0025	11.792	0.8923	1.89E+14	0.0832	0.8482
Cr ³⁺ - SGT	6.00E-06	17.86	0.7418	0.216	1.2564	0.9541
Cr ⁶⁺ - NGT	2.00E-05	22.47	0.5688	1.451	0.0116	0.474
Cr ⁶⁺ - SGT	2.00E-04	50.251	0.6927	6.71E-01	3.6976	0.5826

Table 5: Weber-Morris and film diffusion parameters for Cd²⁺, Cr³⁺ and Cr⁶⁺ onto NGT and SGT

Adsorption Kinetics	Weber-Morris Model			Film diffusion Model	
	k _{ad}	C	R ²	R ¹	R ²
Cd ²⁺ -NGT	0.0911	1.2148	0.7527	0.0585	0.2291
Cd ²⁺ -SGT	0.7289	44.89	0.4852	6.80E-03	0.0288
Cr ³⁺ -NGT	0.0282	2.636	0.7596	0.0776	0.4818
Cr ³⁺ -SGT	0.4327	25.686	0.8823	0.0643	0.2467
Cr ⁶⁺ -NGT	0.0043	2.3155	0.522	0.0016	0.019
Cr ⁶⁺ -SGT	1.1234	9.0149	0.4154	0.0992	0.7326

It was observed from Table 3 that the pseudo-first order model was fairly obeyed only in Cd²⁺-SGT (R² = 0.6755) and Cr⁶⁺-SGT (0.7326). The good fittings to sorption of Cd²⁺ and Cr⁶⁺ ions onto SGT could signify that one adsorbate ion was sorbed onto one sorption site on the surface of the adsorbent.

Table 3 also revealed that the removal of Cd²⁺, Cr³⁺ and Cr⁶⁺ ions by both adsorbents fitted very well into the pseudo second order model with the R² values being almost equal to unity, which depicts that the adsorption processes were chemisorption in nature. Similar results were also observed by [25], [46], [19]. Thus, it can be concluded that the adsorption of the metal ions followed pseudo-second order model more perfectly than the pseudo-first order which showed that the adsorption processes proceeded by chemisorption mechanism (rate determining step) [47].

The results obtained in Table 4 showed that second order model fitted fairly well in the adsorption processes with a relatively higher R² values for all metal ions on SGT. The good fittings signified that adsorption process occurred via chemisorptions mechanism.

In a similar manner, the Elovich model was fitted well in the adsorption of Cd²⁺, Cr³⁺ ions onto both adsorbents, and Cr⁶⁺ on SGT as evident from their R² values. The good fittings signified that the adsorption processes occurred via chemisorptions mechanism [43].

From Table 5, it was observed that the closeness to unity of the correlation coefficients from the Weber-Morris plot for Cr³⁺-SGT (R² 0.8823) showed good fittings to the

intraparticle diffusion model, indicating that Cr³⁺ ions diffuse from the outer surface into the pores of the adsorbents. That of Cd²⁺-NGT (0.7527), Cr³⁺-NGT (0.7596) and Cr⁶⁺-NGT (0.522) is only fairly accepted. The remaining adsorption systems; Cd²⁺-SGT (0.4852) and Cr⁶⁺-SGT (0.4154) showed poor fittings to this model. The Weber-Morris plots in all the adsorbates studied were linear and failed to go through the origin, an indication that intra-particle diffusion was not the sole rate determining step and that the rate of adsorption may also have been controlled by some other mechanisms [48].

From the results obtained in Table 5 for film diffusion, it was observed that the value of correlation coefficient (R²) was only fairly close to unity for Cr⁶⁺ on SGT, indicating good fitting to this model whereas, the remaining adsorption systems showed very poor fittings. However, all plots obtained for film diffusion model failed to go through the origin. Based on this and the lower R² values obtained for most adsorption systems, it can be concluded that the rate controlling step may not be only film diffusion or intraparticle diffusion process or that other processes occurred simultaneously with these processes in the mechanism of the adsorption [34], [49].

3.4 Comparison of different adsorbents for the removal of Cd²⁺, Cr³⁺ and Cr⁶⁺ from aqueous solution

Table 6 shows the comparison of equilibrium adsorption capacities, q_e (mg/g) obtained as parameter from best fitting kinetic model for the sorption of Cd²⁺, Cr³⁺ and Cr⁶⁺ ions onto different adsorbent materials.

Table 6: Comparison of equilibrium adsorption capacities for different adsorbent materials

Adsorbent	q _e (mg/g)			Author (s)
	Cd ²⁺	Cr ³⁺	Cr ⁶⁺	
Raw date pits	6.02	-	-	[50]
Activated date pits	17.24	-	-	[50]
Goethite nano particle	59.52	-	-	[51]
Red rose waste biomass	-	80.22	110.24	[52]
Sugarcane pulp residue	-	3.482	0.601	[53]
ZIF-8	-	-	0.15	[54]
ZIF-8/NH ₂ /Mg(OH) ₂ /GO	-	-	4.88	[54]
NGT	1.69	2.935	2.369	Present study
SGT	51.81	30.12	21.19	Present study

4. Conclusion

From the adsorption data, the sorptive property of the natural goethite and synthetic goethite was found to be dependent on agitation time. The kinetic modeling revealed the order of fittings; Pseudo-second order > Elovich > Second order > Pseudo- first order, as well as intra-particle diffusion > film diffusion. The adsorption proceeded by a chemisorption process as suggested by the Pseudo-second order, second order and Elovich models and that the mechanisms of the adsorption occurred by more than one process; either intra-particle and film diffusion, or that other processes occurred simultaneously with these two processes in the mechanism of the adsorption but certainly more of the intra-particle diffusion. Therefore, the results obtained from this study could provide resourceful information on Cd²⁺, Cr³⁺ and Cr⁶⁺ fixation onto goethite particles, and certain industrial applications.

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