Research Article

Treated Clay Mineral as Adsorbent for the Removal of Heavy Metals from Aqueous Solution

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Abstract

The decontamination of heavy metals present in aquatic bodies is a significant challenge that requires urgent attention. Analytical methods such as BET, XRF, SEM-EDX, and XRD was employed to characterize the raw clay (NT) and acid treated clay (AT). The adsorption of Cr (VI) and Fe (III) onto AT was performed using the batch method. The effects of time, adsorbent dose, temperature, and pH show that the optimal conditions are 50 min, 0.3 g, 35°C, and pH 6. The surface area of AT was 389.37 m^2/g, and the adsorption equilibrium time of AT was 50 min. Langmuir isotherms had the best fit. Adsorption capacity is 18.15 and 39.80 mg/g for Cr (VI) and Fe (III) ions, respectively. An increase in area considerably improved the adsorption capacity of AT in the surface specific area. The interaction of Cr (VI) and Fe (III) ions onto AT indicated spontaneous and endothermic reaction. The chromium (VI) kinetic constant ($k_2 = 1.679$) was faster compared to Fe (III) rate constant ($k_2 = 0.0526$). It agreed correctly with the pseudo-second-order equation. The sum square error (SSE) value obtained confirmed the best-fit equations. The percent adsorbed for Cr (VI) and Fe (III) is 74 and 90%. The results revealed that iron has a higher affinity towards AT than chromium. The study revealed that AT could be suitable and effective in the adsorption of chromium and iron in the wastewater medium.

Keywords: Reated clay, Kinetic, Isotherm, Thermodynamic, Adsorbent, Chromium, Iron

1 Introduction

The heavy metals present in water bodies above the acceptable limit are severe hazards to humans and ecosystems. They are non-biodegradable and can persist in different environmental conditions. Therefore, this calls for urgent attention for adequate treatment and regulations concerning the amount of chromium (VI) and iron (III) present in the aquatic medium. The permissible limit for chromium and iron is 0.1 and 0.3 mg/L as recommended by the United States Environmental Protection Agency (USEPA) [1]. Therefore, to keep the public and their environment safe, it is necessary to remove these pollutants from the aquatic ecosystem.

The primary source of ferric metallic ions is the ore mining activities, which comprises various minerals and heavy metals. The mining waste at an oxidized state is corrosive and leads to acid mine drainage. It contains arsenic, copper, lead, cadmium, iron, and sulfates. Ferric ions are highly present in acid mine drainage waters in a concentration of several 100 mg/L [2], [3]. Therefore, it is essential to treat any ferric ion

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contaminated water to a permissible level of 0.3 mg/L based on appearance and taste [4]. Excess iron in the human body can cause anorexia, oliguria, diphasic shock, hemochromatosis, diabetes mellitus, liver cancer, and cirrhosis [5], [6].

Chromium is used widely in chrome plating, pigment, textile, wood preservation, and an antifouling agent in cooling towers [7]. Chromium (VI) ion present in water above the permissible limit is poisonous. It can cause diseases like cancer, kidney, and liver failure [8]. Therefore, it necessary to treat any wastewater containing chromium (VI) to the permissible level. According to WHO, the permissible limit for water fit for human consumption is 0.05 mg/L, and wastewater is 0.5 mg/L [9]. Removal of Fe (III) and Cr (VI) in wastewaters is a significant challenge. Different types of traditional and non-traditional resources were employed to adsorb various metals [10]. They include, chromium and nickel [11]–[13], iron (II) and (III) [2], [5], [14]–[16].

However, several studies have reported industrial effluent treatment containing heavy metals using either natural or modified clay. Different types of clays and their minerals played a vital role in the environment. They are often employed to serve as effective adsorbent suitable for treating water contaminated with harmful heavy metals [17]. They are low-cost natural adsorbents, highly porous, large active sites, good adsorption characteristics, excellent cation exchange capacity and available naturally. They are non-toxic to the ecosystem [18].

The application of clay minerals as an adsorbent has advantages compared to other traditional and non-traditional adsorbent available. Clay is relatively cheap compare to ion exchange resin, synthetic and natural zeolites and activated charcoal. Clay surfaces contain both cations and anions which are readily exchangeable. These advantages of clay minerals have generated interest from researchers globally to shift their attention to the use of treated clay materials in treating industrial wastewater [19].

Nigeria has a large deposit of clay, which have many significant uses in different industries. Therefore, there is a need to look inward in harnessing the local resources in providing solutions to challenges obtainable in various industry. Considering the economic and environmental safety, clay mineral is used for water treatment because it is easily affordable and environmentally friendly. Therefore, it becomes necessary to improve the adsorption capacity and expand local clay application beyond fine art and local pottery work. The sourcing of natural material from local sources will support the local economy and help lower environmental impact. The results of this study will definitely encourage the use of Nigerian local resources and content in providing benefits and solutions to the problems confronting local industries. To date no report on the use of the local clay for the adsorption of chromium and iron in real industrial textile wastewater.

This study will remove selected heavy metals such as Cr (VI) and Fe (III) from wastewater using hydrochloric acid treated clay. This clay is found naturally in abundance locally in Anambra, Nigeria. However, most literature reports are mainly on the treatment of simulated wastewater. This study is the first to employ hydrochloric acid-treated clay sourced locally to remove selected heavy metals in real industrial wastewater.

Therefore, the study will aim to prepare and evaluate treated clay in comparative adsorption of iron and chromium in a real industrial effluent. The adsorption of Cr (VI) and Fe (III) ions onto modified natural clay from a local source was by batch adsorption. Furthermore, factors like time, pH, amount of clay, temperature, and the isotherms, kinetics, and thermodynamic data were studied.

2 Materials and Methods

2.1 *Preparation and characterisation of adsorbent*

Non-treated clay (NT), sourced in Umunze, Anambra State, Nigeria, was treated with acid (HCl) and was denoted as (AT). 50 g of NT was dissolved in 100 mL of 4N HCl solution [20], [21] and stirred continuously for 1 h and left for 24 h. At the end it was decanted, and washed thoroughly with distilled water. The filtrate was dried in an oven for 4 h at 110°C. It was cooled, milled, and sieved to particle sizes of approximately 125 um and kept in a safe place for further used. The reagents were used as received.

A textile industry supplied the effluent used for analysis. The properties of wastewater were characterized, according to the American Public Health Association standard [22]. The parameters analysed were pH, chemical oxygen demand (COD), alkalinity, and biochemical oxygen demand (BOD). The amount of nitrate and ammonium, electrical conductivity, dissolved oxygen (DO), and total dissolved solids (TDS) [22]. The heavy metals in wastewater were analysed using the Atomic Absorption Spectrophotometer (AAS) PG 990 model.

The surface area analyser of model ASAP 2020, measured the textural properties of NT and AT. SEM-EDX (JEOLJSM 7600F) determined the morphology and elemental composition. Thermo Electron Nicolet 4700 FTIR spectrometer, recorded the spectra of the adsorbent from 4000 to 500 cm^{-1} resolution. X-Ray Fluorescence (XRF) and XRD were carried with a PW2400 and MD 10 Randicon diffractometer, respectively. The pHpzc was measured as reported [23]. The cation exchange capacity (CEC) of adsorbent was done, as described by Hattab *et al*. [24].

2.2 *Adsorption study*

Chromium (VI) and iron (III) ions adsorption was conducted with batch method. 0.1 g of AT was mixed with 50 mL of wastewater. The mixture at a temperature of 27°C was agitated at 190 rpm for 120 min, filtered. It was analyzed with the atomic absorbance spectrophotometer (AAS). The parameters were studied with the following experimental conditions. Contact time used are 10, 20, 30, 40, 50, 60, 90, and 120 min, adsorbent dose used are 0.1, 0.2, 0.3, 0.4 and 0.5 g, pH values was tested from 2 to 12 and temperatures were 25, 30, 35, 40 and 45°C.

The quantity q_e (mg/g) of heavy metals removed was determined by Equation (1),

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Where C_0 (mg L^{-1}) is the initial concentrations of metal ions. C_e (mgL^{-1}), as equilibrium concentration, V (L) is the volume of the solution, and W (g) is the mass of dry adsorbent. Removal efficiency (R) of metal ions was calculated by Equation (2):

$$\%\, R = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

Where C_t (mg L^{-1}) is the concentration of metal ions at a time, t.

2.3 *Desorption study*

A batch desorption study was carried out to test the recoverability of adsorbent. It was done with H_2SO_4 as regenerant. 30 mL of 0.5 M solution was mixed with adsorbent after the adsorption process. The mixture was shaken at 180 rpm for 90 mins, after which the sample was analyzed for desorbed metal concentration [25].

2.4 *Error analyses*

To ensure the correctness of fit (R^2) of the models. The error function method of sum square error (SSE) was employed to confirm the best-fit isotherm and kinetic models, to represent the process is Equation (3) [26].

$$SSE : \sum_{i=1}^{n} (q_{e,cal} - q_{e,\exp})_i^2 \tag{3}$$

The experimental value is represented as $q_{e,exp}$, the calculated value as $q_{e,cal}$, and the number of data points (n).

3 Results and Discussion

3.1 *XRF analysis*

The XRF analysis of the NT and AT was presented in Table 1. The main constituents in the NT are silica (SiO_2) and alumina (Al_2O_3) with an approximate percentage of 67.82 and 12.88%. Others are impurities which include the oxide of Fe, Ca, Mg, K, Ti, Na and Mn [27]. It can be seen that Al_2O_3, Fe_2O_3, MgO, CaO contents decreased and silica (SiO_2) increased slightly with activation. These changes showed that clay in its natural form is resistant to acid attack [28]. The increase in adsorbent surface area may be due to changes undergone by its structure in the acidic medium [29]. Also, the increase in surface properties may result from the destruction and transformation of clay mineral structure. This may result in the generation of fine silica particles, the formation of voids and cracks or removal of silica or aluminium on the surface [20].

Table 1: Chemical characterization of NT and AT

Content	Weight (%) NT	Weight (%) AT	Weight (%) [27]
SiO_2	67.82	70.27	76.4
Al_2O_3	12.88	12.32	13.6
Fe_2O_3	6.68	5.17	6.65
TiO_2	1.48	1.42	1.34
CaO	0.36	0.24	2.20
MgO	1.50	1.17	1.06
Na_2O	0.15	0.16	0.06
k_2O	0.51	0.49	0.27
MnO	0.14	0.02	0.00
LOI	7.92	7.79	4.5

It suggests that acid modification has depleted the octahedral and interlayer and cations, affecting adsorbent efficiency [30]. After activation, there was a decrease in the number of cations like Al^{3+}, Fe^{3+} and Mg^{2+}. This suggests that cations such as K+, Na+ and Ca^{2+}, have been replaced with hydrogen ions. Others like Al^{3+}, Fe^{3+} and Mg^{2+} were leached from the tetrahedral octahedral sites, which exposes the edges of the clay particles [31]. The high mineral content and low carbonaceous matter of the adsorbents conformed with the value of a loss on ignition obtained is 7.92 and 7.79 % for the NT and AT, respectively [32].

3.2 *BET analysis*

As exhibited by clay materials, the adsorption tendency is due to their corresponding available surface area [33]. Many researchers have shown that the relationship existing between the clay available area and its adsorption ability is directly proportional [34]. The surface area and pore volume of AT is 389.4 and 0.217 mL/g, respectively (Table 2). Acid treatment caused more surface creation, which resulted to about 4:1 ratio increment compared to NT (84.22 m^2/g and 0.053 mL/g). The exchange of cations and silica generation resulted from acid treatment led to an increment in the available surface area of NT [35]. It can also be due to the removal of the impurities (Tables 1 and 2) [36].

Acid treatment increased the CEC of NT (8.4 cmol/g) to (22.3 cmol/g) for AT (Table 2), which resulted to about three times increase in the available active site. This increment resulted from broken bonds, hydroxyl transfer, and clay structure defect related to ion exchange capacity [37]. The CEC of NT and AT is 8.4 cmol/g and 22.3 cmol/g, respectively. Based on CEC, the adsorbent value increased after activation [24].

Table 2: Result of BET analysis

Samples	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	CEC (cmol/g)
NT	84.22	0.053	2.115	8.4
AT	389.4	0.217	2.487	22.3

3.3 *SEM analysis*

The result of the adsorbent microstructure as analyzed with SEM is shown in Figure 1. The effect of activating agents in the structures show significant changes after activation. AT has an irregular, rough, porous, and heterogeneous structure that is a suitable property of an adsorbent [38], which can aid molecular transport. This report is consistent with the literature on the modification of clay [39], [40].

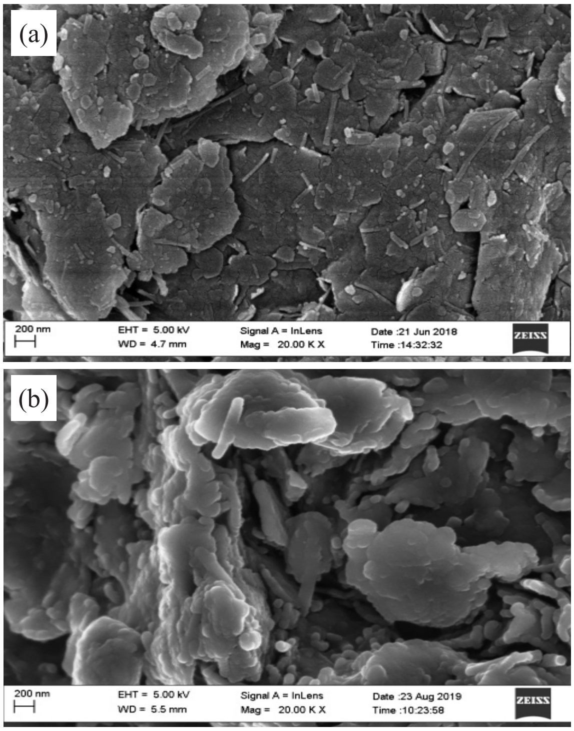

Figure 1: SEM images of (a) NT and (b) AT.

3.4 *XRD analysis*

Figure 2 show the spectra of NT and AT. The prominent peaks at 2θ = 25.2° and 28.65°, 30.2° and 53.45°, the peaks indicate the presence of three rigid dimensional framework which consist of inter linked quartz (SiO_2). The peaks at 2θ = 21.41°, 36.13°, 41.45°, 45.70°, 60.21°, 68.32° indicates the presence of properties of kaolinite clay. Montmorillonite peaks are observed to have disappeared after acid modification [41]. The appearance of more kaolinite is an indication of the increase in the pore size of AT. This could be explained as follows, and the chemical agents exposed the tetrahedral layer by attacking the octahedral layer. The transformation of the crystalline structure of clay which leads to a decrease in peak intensity [42].

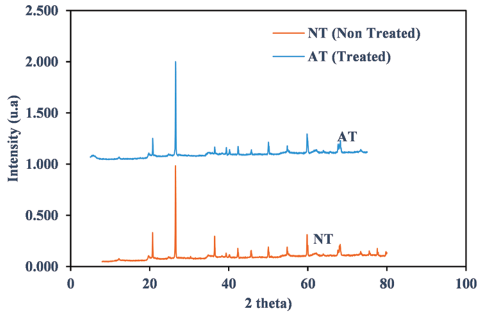

Figure 2: XRD pattern of NT and AT.

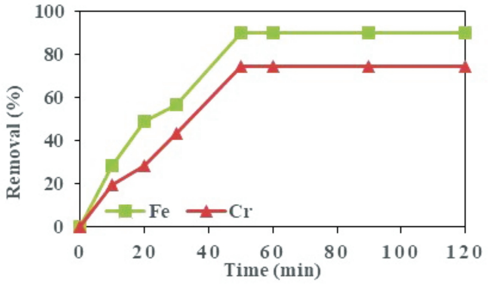

Figure 3: Effect of contact time on adsorption of Cr (VI) and Fe (III) onto AT.

3.5 *Physicochemical properties of wastewater*

The results of the physicochemical properties of raw wastewater (RW) and treated wastewater (TW) are presented in Table 3. As shown in Table 3, the pH of wastewater 10.2 declined to 7.95 after treatment. This is in agreement with the standard. According to WHO, the pH of wastewater and drinking water is in the pH range of 6.5–8.5 and 7. [43], [44]. The electrical conductivity of wastewater is >1000 µS/cm indicates contaminated water. Thus, there is a need to make it up to the standard level [45]. After the treatment of wastewater with AT its value reduced significantly (Table 3) within the WHO standard and National Environmental Standards Regulatory and Enforcement Agency [44].

Table 3: Physicochemical properties of wastewater before and after treatment with AT

Parameters	RW	TW	WHO
pH	10.2	7.95	5.5–8.5
TDS	1085	531	600
Conductivity (µS/cm)	2380	793	1000
DO (mg/L)	3.90	5.10	5–6
Turbidity (NTU)	3.72	2.00	5.0
Alkalinity (mg/L)	120	26	-
Nitrate (mg/L)	896	17.7	50
COD (mg/L)	218	15.0	40
BOD5 (mg/L)	30.5	18.0	15
Ammonium (mg/L)	11.20	5.92	1.5
Cadmium (mg/L)	0.151	0.025	0.003
Chromium (mg/L)	0.278	0.0713	0.050
Iron (mg/L)	0.748	0.0754	0.300

Dissolved oxygen is one of the most crucial parameters to be considered in measuring water quality. The deficiency of dissolved oxygen will promote the formation of as hydrogen sulfide in the presence of organic materials and sulfate. After treatment, the dissolved oxygen changed from 3.11 mg/L to 5.10, which falls within NESREA [44] and WHO [45] standards. Biochemical and chemical oxygen demands are useful for assessing the quality of effluent. The presence of inorganic and organic components in wastewater could be responsible for the high values. As recommended by WHO the limits of 15 mg/L and 40 mg/L are acceptable for aquatic life. The heavy metals present over permissible limit decreased to the following values, cadmium (0.025), chromium (0.071) and iron (0.075). After treatment with AT the targeted contaminants were reduced entirely to an acceptable limit.

3.6 *Adsorption study*

3.6.1 Effect of time

Chromium (VI) and iron (III) adsorption is affected by time, as shown in Figure 3. The adsorption process was performed with a time range of 10–120 min, at dosage 0.3 g, pH 6 and 25°C room temperature. As shown in Figure 3, at the initial stage, metal adsorption shows a rapid increase with time up to equilibrium at 50 min. The percentage removal of iron (III) and chromium (VI) increased with contact time. The kinetics of sorption was fast for 50 min. The percentage metal ions removed at equilibrium time are 74.39 and 89.93% for Cr (VI) and Fe (III).

The rate of metal ions adsorption onto AT happened quickly, as a result the movement of the ions from liquid phase to active adsorption site becomes rate dependent. The higher rate of adsorption at the initial stage could be attributed the presence of empty active area sites

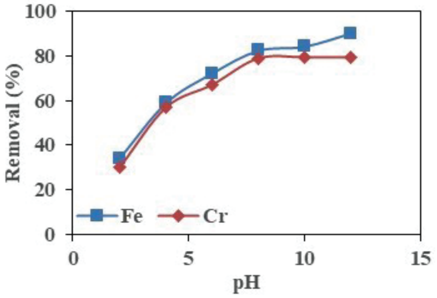

Figure 4: Effect of pH on adsorption of Cr (VI) and Fe (III) onto AT.

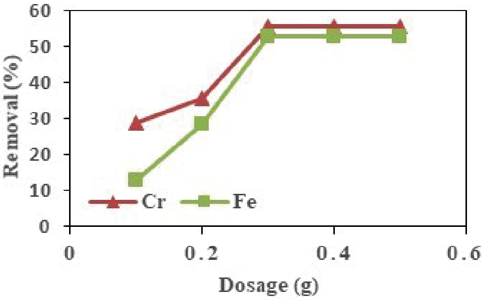

Figure 5: Effect of adsorbent dosage on adsorption of Cr (VI) and Fe (III) onto AT.

on AT. However, the contact time increased and metal adsorption slows down, until the all sites were filled up completely. The adsorption equilibrium was attained very fast and this suggests that the dominant mechanism for adsorption of Fe (III) and Cr (VI) onto AT is complexation and chemical adsorption [46].

3.6.2 Solution pH effect

The pH was varied from 2 to 12, at 190 rpm, a dose of 0.3 g, time of 120 min and 25°C, this is represented in Figure 4. The metal ion adsorption increased with the pH for both adsorbates.

The change in the pH from 2 to 6 caused an increase in Cr (VI) (30–79 %) and Fe (III) (34–90 %) removal, and this suggests the optimum pH is 6. The removal of metal ions shows a steady increase with the pH value for both ions until pH 6. Beyond this point, Cr (VI) ion becomes steady, and Fe (III) show a sudden rise in adsorption. The increase in Cr (VI) and Fe (III) adsorption within an acidic medium may be attributed to the electrostatic attraction between positively charged groups of clay surface and oxyanions of Cr (VI), i.e., $HCrO_4^-$ anion and $Fe(OH)^{3+}$, were the dominant species [47].

At low pH, Fe (III) and Cr (VI) ions were competing with hydroxonium ions for available active sites, and this caused low adsorption of Fe (III) and Cr (VI). At higher pH, the active sites gradually become deprotonated and resulted to high adsorption of metal ions. This is because clay surface has active sites that possess weak acidic properties [47]. Different mechanism such as ion exchange, chemical complexation and electrostatic forces could be responsible for metal ions removal [48].

As mentioned earlier, the adsorption was maximum at pH 6.0, beyond this point Cr (VI) removal was constant. While Fe (III) shows a moment of still and a sudden rise [49]. This can also be attributed to the effect of competition from other contaminant present in the effluent. As well as the precipitation of complexes of chromium, $Cr(OH)_3$ and iron, $Fe(OH)_3$ at pH beyond 6. This may have blocked the movement of some metal ions into adsorbent surface leading to adsorption and co-deposition. The insoluble complexes of precipitated metal hydroxides may appear as apparently higher metal ion removal [50], [51]. Furthermore, at higher pH the adsorbed metal ions may be due to precipitate of hydroxides [52].

3.6.3 Adsorbent dose effect

Figure 5 show the effect of amount of adsorbent as varied from 0.1–0.5 g, at contact time of 50 min, pH 6 and 25°C. The amount of adsorbent increased with removal percent of metals, until it reached 0.3 g. It increased from 29.09–45.69.0% for Cr (VI) and 12.78–42.86% for Fe (III) respectively. The percentage adsorption increased between 0.1 and 0.3 g; the dose increased the availability of adsorption sites. This suggests the optimum dosage is 0.3 g. However, beyond this value, Cr (VI) and Fe (III) were few in the reaction medium to interact with available surface area, since almost all ions are adsorbed. Hence the adsorption became constant, and additional adsorbent made no significant contribution [53].

3.6.4 Temperature effect

Chromium (VI) and iron (III) adsorption onto AT as

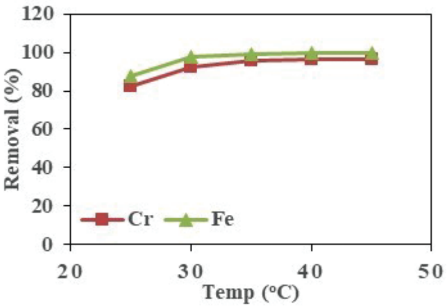

Figure 6: Effect of temperature on adsorption of Cr (VI) and Fe (III) onto AT.

affected by temperature is shown in Figure 6. It shows metal ions adsorption increased from 25 to 30°C, (87.49–97.56%) for Fe (III) and (82.37–92.35%) for Cr (VI). It could be due to the increased kinetic effect, thus increasing the adsorbates molecule's mobility as temperature increased. The high adsorption recorded indicates the process is endothermic. A further increase in temperature beyond the optimum temperature of 35°C had an insignificant effect. The percent removal of Fe (III) and Cr (VI) was 99.91% and 96.32%. This is the penetration of vacant active sites due to temperature rise; this suggests endothermic reaction [40], [54].

3.6.5 Point of zero charge

Information on the point where charges are zero (pHpzc) will enable us to know whether an adsorbent surface possesses a positive or negative charge. pHpzc measurement to determine the nature of their surface charge (Figure 7). The isoelectric pH for AT is 3.48 (acidic), and NT is 7.85 (basic). Due to acid treatment, the isoelectric pH decreased from 7.85 to 3.48. This indicates that AT would be suitable and applicable in removing metal ions at pH > 3.48 [24]. In principle, when the pH of any substance is less than the pHpzc, the sample develops more positively charged, making it a favourite material for the adsorption of anions. Conversely, suppose the pH is greater than pHpzc. In that case, the samples develop a more negative charge, making it the favourite material for cations' adsorption [23], [55].

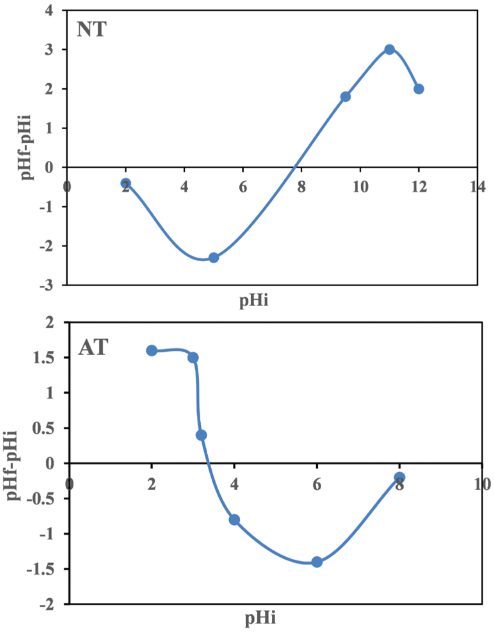

Figure 7: Point of zero charge for (a) NT and (b) AT.

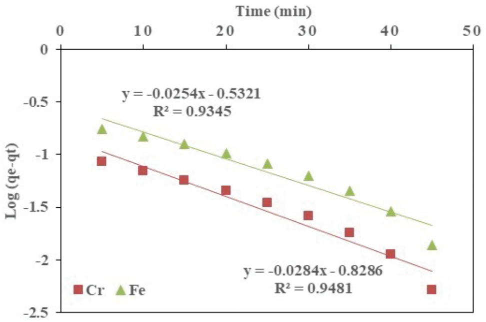

Figure 8: Pseudo-first order kinetic for adsorption Cr (VI) and Fe (III) onto AT.

3.7 *Kinetic study*

The first-order, Equation (4) and second-order, Equation (5) were used to understand the dynamics of kinetic data with respect to time. As presented in Figure 8 and, Table 4, the R^2 value of 0.95 and 0.96 for Cr (VI) and Fe (III) were obtained for the first-order model. While R^2 values of pseudo-second-order on adsorbent were 0.99 and 0.99 for Cr (VI) and Fe (III) (Figure 9 and Table 4). This high coefficient of determination value confirmed with the equation of second-order [6], [16], [56], [57]. The higher coefficient of determination (R^2) value from Table 4 shows that the SSE value was lowest for the second-order equation compared to the first order. The second-order equation is the most appropriate to describe the process. The main mechanism is chemical adsorption onto AT.

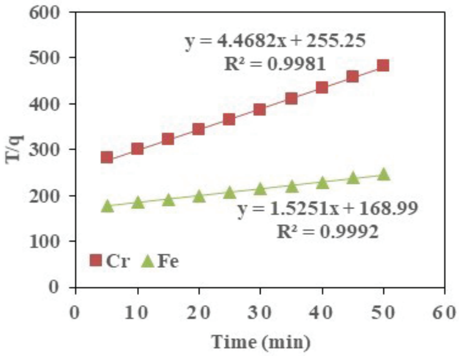

Figure 9: Pseudo-second order kinetic for adsorption Cr (VI) and Fe (III) onto AT.

$$\ln\left(\frac{q_e}{q_t}\right) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Where q_t is the amount of metal ions adsorbed (mg/g) at given time t (min), q_e (mg/g) is the amount adsorbed at equilibrium; k_1(min^{-1}) and k_2 (g.mg^{-1}min^{-1}) are the constants of first and second-order rate equation.

Table 4: Kinetics models for adsorption Cr (VI) and Fe (III) onto AT

Pseudo-First-Order Kinetics					
Metal Ions	**$q_e$exp (mg/g)**	**$q_e$cal (mg/g)**	**k^1 (min^{-1})**	**R^2**	**SSE**
Cr (VI)	0.1034	0.4367	0.0654	0.94	0.1111
Fe (III)	0.2030	0.3504	0.0707	0.93	0.0217
Pseudo-Second-Order Kinetics					
Metal Ions	**$q_e$exp (mg/g)**	**$q_e$cal (mg/g)**	**k^1 (min^{-1})**	**R^2**	**SSE**
Cr (VI)	0.0713	0.0729	1.679	0.99	2.56E-6
Fe (III)	0.2030	0.1334	0.526	0.99	0.00484

From Table 4, the constant of the second-order equation is higher than that of the first-order equation. This suggests enhanced molecular mobility, which is favourable for mass transfer in porous solids. This behaviour is common in porous media like activated carbon and zeolites [58]. This also indicates that chemisorption is the rate that determine the steps in the kinetic adsorption reactions. This confirmed pseudo-second-order equation had best fit; and are consistent to other reports in the literature [59].

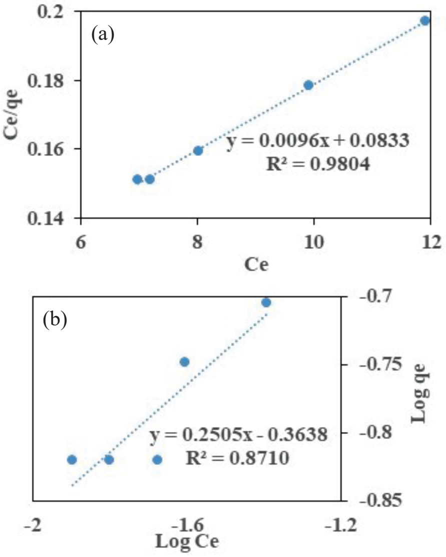

Figure 10: (a) Langmuir and (b) Freundlich Isotherm for Cr (VI) adsorption onto AT.

3.8 *Isotherm study*

The equilibrium isotherm data for adsorption of Cr (VI) and Fe (III) onto AT was analysed with Langmuir, Equation (6) and Freundlich, Equation (7). To determine how effective an adsorbent could be the value of separation factor (RL) was used, this is defined as represented in Equation (8). The plots of isotherms and evaluated parameters are shown in Table 5 and Figures 10 and 11. High coefficient of determination (R^2) values signified the appropriateness of Langmuir isotherm data than Freundlich. The interactions occurred on a monolayer surface for all identical sorption sites [60]. The highest removal recorded for Cr (VI) and Fe (III) is 18.15 and 39.80 mg/g. This suggests their suitability to decontaminate polluted aqueous medium. Table 6 presents the comparison of clay materials and their adsorption capacity for the studied metals. The adsorption is favourable because all the RL obtained lies between zero and one ($0 < R_L < 1$) [61]. The higher R^2 (Table 5 and Figure 9 and 10), further confirmation was made on the isotherm and kinetic models using error analysis, SSE values support the R^2 (Table 5), this further suggests that Langmuir model is very suitable, this is similar to the finding [26].

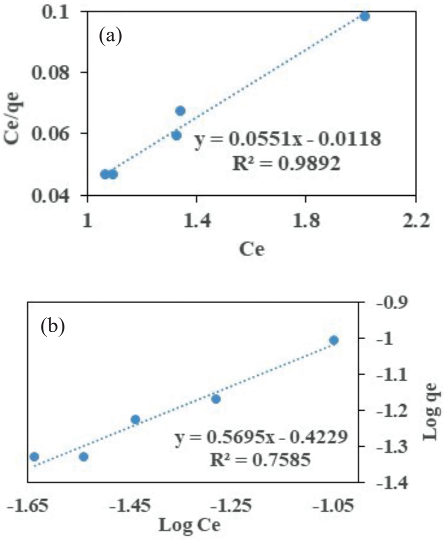

Figure 11: (a) Langmuir and (b) Freundlich Isotherm for Fe (III) adsorption onto AT.

Table 5: Isotherm parameters for adsorption Cr (VI) and Fe (III) onto AT

Isotherm Parameter	Metals	
	Cr (VI)	Fe (III)
Langmuir		
q_m (mg/g)	18.15	39.80
K_L (L/g)	0.056	0.028
R_L	0.984	0.979
R^2	0.9804	0.9892
SSE	0.01137	0.00045
Freundlich		
K_F (mg/g) (L/mg)	1.526	7.264
n	1.76	0.356
R^2	0.8710	0.7585
SSE	0.0135	0.00345

Table 6: Adsorption capacity of clay materials towards Cr (VI) and Fe (III)

Adsorbent	Metal Ion	Langmuir q_m (mg/g)	References
AT	Fe (III)	39.80	This study
Natural clay	Fe (III)	5.7	[62]
Activated clay	Fe (III)	30	[6]
Naturalfeldspar	Fe (III)	25	[57]
AT	Cr (VI)	18.15	This study
Kaolin	Cr (VI)	11.60	[63]
Sepiolite	Cr (VI)	27.05	[64]
Treated clay	Cr (VI)	8.77	[65]

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

Based on the value of R_L, isotherm can be classified, as favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), reversible ($R_L = 0$) or linear ($R_L = 1$). Where q_e (mg/g) is the amount of metal ion adsorbed, qm, represents a complete monolayer adsorption of metal ions (mg/g), and K_L (L/mg) is the Langmuir constant. Where K_F (mg/g) (L/mg) and n are the Freundlich constants.

3.9 *Thermodynamic study*

Thermodynamic parameters depend on the reaction process. They can help in the detailed study of the adsorption process mechanism. The standard entropy (ΔS^o) (kJ/mol k), enthalpy (ΔH^o) (kJ/mol), and free energy (ΔG^o) (kJ/mol) for adsorption of metals onto adsorbents were determined with Equations (9)–(11). Equation (11) was applied to analyse ln K against 1/T plot, the slope obtained as enthalpy (ΔHo) and intercept as the entropy (ΔS^o), respectively. It was examined at different temperatures of 25, 30, 35, 40, and 45°C (Table 7). The value of enthalpy change (ΔH^o) is positive, which indicates an endothermic process. The enthalpy of Cr (VI) and Fe (III) onto adsorbent are 26.3 and 36.1 kJmol^{-1} respectively. This suggests the interaction of metal ions with activated clay is endothermic [6]. The entropy change (ΔS^o) is positive, and it was measured at 298K for Cr (VI) and Fe (III), as 0.058 and 0.159 KJmol^{-1}K^{-1}. The values of Gibbs energy (ΔG^o) were all negative, the entity measures the spontaneity of a reaction process. From Table 7, it can be seen that as temperature increased, the free energy also increased [56]. This indicates a favourable and spontaneous endothermic reaction [66].

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{9}$$

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

$$\Delta G^o = -RT\ln K_c \quad (11)$$

Table 7: Thermodynamic parameters of adsorption Cr (VI) and Fe (III) onto AT

Metal Ions	Temp (K)	ΔH^O ($kJmol^{-1}$)	ΔS^O ($KJmol^{-1}K^{-1}$)	ΔG^O ($kJmol^{-1}$)
Cr	298	26.30	0.0578	–0.9236
	303			–1.2127
	308			–1.5017
	313			–1.7907
	318			–2.0798
Fe	298	36.08	0.1591	–11.3471
	303			–12.1428
	308			–12.9386
	313			–13.7344
	318			–14.5302

3.10 *Desorption study*

The desorption process was done to increase the economic value of the adsorbent, a batch process tested its recoverability. The study results on AT to determine the amount of metal ions released are presented in Table 8. It can be seen that tetraoxosulphate (VI) acid showed a maximum desorption efficiency of 92.45 and 95.62% for Fe (III) and Cr (VI), respectively [25].

Table 8: Percentage desorption efficiency using H_2SO_4 desorbing agent

Adsorbates	% Desorption
Cr	95.62
Fe	92.45

4 Conclusions

The treatment of clay with HCl acid for Cr (VI) adsorption and Fe (III) was performed. The study has shown that AT is an economical and useful material in adsorption of chromium (VI) and iron (III) wastewater medium. The surface area analysis of NT revealed the increase in surface area of after treatment with acid. After treatment, the surface area increased from 84.223 m^2/g (NT) to 389.37 m^2/g (AT), total pore volume from 0.00527 to 0.2168 cm^3/g, respectively. This result is consistent with SEM-EDX studies which shows the formation of rough surface and porous structure. AT adsorbent has pHpzc and CEC values of 3.48 and 22.3 cmol/g. The analysis of isotherm data as performed with the Langmuir and Freundlich model, indicated that Langmuir model had the best data description. The R^2 values confirmed second-order equation as the appropriate model. This was supported by the lowest SSE error value obtained. The highest adsorption capacity recorded for Cr (VI) and Fe (III) are 18.15 and 39.80 mg/g, maximum desorption efficiency of 92.45 and 95.62% for Fe (III) and Cr (VI) was obtained respectively. Treated clay is cheap and available, can be useful as alternative adsorbent in decontamination of chromium and iron polluted wastewater.

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