

Sorption Performance of Activated Nkaliki Clay in Removing Chromium (VI) Ion from Aqueous Solution: Kinetics, Isotherm, and Thermodynamic Studies

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Summary: Bentonite from Nkaliki was modified by acid activation using different concentrations of sulphuric acid. The physicochemical properties of the raw and modified samples were analyzed. The sorption performance of the modified and raw bentonite was studied in the removal of chromium (VI) ion from aqueous solution. Effect of key process parameters on the adsorption process was studied. Results of the physicochemical analyses showed that the acid activation altered the structural arrangements of the bentonite. The surface area and adsorption capacity increased from 37.6m²/g to 74m²/g and 45 to 98%, respectively, after activating with 6mol/l of H₂SO₄. The chromium (VI) ion adsorption increased with increase in process parameters studied. The kinetics analysis of the adsorption data follows the pseudo second-order kinetics, while equilibrium analysis conformed to the Langmuir isotherm. The thermodynamic parameters revealed that adsorption process is spontaneous and endothermic. This study shows that modified Nkaliki bentonite could be used for wastewater treatment.

Keywords: Acid activation; Adsorption; Physicochemical properties; Kinetics; Isotherm; Thermodynamics.

Introduction

Clays are finding increasing application in wastewater as adsorbents due to their low-cost and good intrinsic adsorption characteristics, such as high adsorption capacity and large surface area. There are large numbers of clay minerals such as kaolin [1], montmorillonite [2, 3], bentonite [4], clinoptilolite [4], smectite [5], sepiolite [6] and zeolite [7] that are widely used for the cost-effective removal of chemical pollutants from wastewater. Among all these clays, bentonite is one of the most widely used due to its abundant availability and good adsorption characteristics [7]. Adsorption capacity and selectivity of natural and or raw bentonite can be limited. Thus, a systematic surface modification of bentonite is essential for the removal of anionic compounds from wastewater since most of the dissolved chemical pollutants are negatively charged [8]. There are various physical and chemical methods available for the modification of clays. These include acid activation [9], treatment with cationic surfactants [10], thermal treatment [11], pillaring, de-lamination and re-aggregation of smectites [12] and grafting of organic compounds [13]. Among these methods, acid activation is one of the most commonly used modification techniques because it is a simple and low-cost process. Acid treatment of clay minerals, namely fibrous clays, smectites [14] and Kaolinite [15], is widely applied in order to optimize their physicochemical behaviour, aiming better industrial properties. Xianzhen and Chuyi [16] have done acid

treatments with sepiolite, concluding that the silica obtained could be competitive in different industrial ways, with that obtained by precipitation. The acid treatment of clay minerals is usually referred to as acid activation, because it increases the specific surface area and the number of active sites of the solids. This treatment modifies the surfaces of clays by dis-aggregations of particles, possible elimination of mineral impurities and removal of metal-exchange cations. The common commercial use of acid-treated clay minerals is bleaching or de-colourations of oils and in general in the fields of adsorption and catalysis.

This study is aimed at investigating the effect of sulphuric acid activation on the physicochemical properties of local bentonite from Nkaliki. The sorption performance of the activated bentonite was examined in the removal of metal ion from aqueous solution. Effect of some process parameters on the sorption study was also investigated and the adsorption kinetics and equilibrium were analyzed.

Experimental

Materials

The bentonite used in this study was mined at the site at Nkaliki in Ebonyi state, Nigeria,

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separated from dirt that contaminated it and sun-dried for 48 hours. The dried bentonite sample was analyzed to determine its chemical composition and physical properties. The physical properties determined were surface area, cation exchange capacity, density and acidity. Standard stock solution of 1 mg/mL of chromium (VI) was prepared from potassium dichromate.

Methods

Acid Activation

The raw bentonite was treated with sulphuric acid solution of varying concentrations (2, 4, 6, 8, and 10 molL⁻¹) at constant temperature of 363 K. 10g of the raw bentonite was reacted with 100ml of known concentration of sulphuric acid solution in a rotary shaker with temperature and agitation control for 3h. At the completion of the reaction period, the reaction was terminated and the slurry was filtered. The acidified product was then washed severally with distilled water until the filtrate was free of sulphate ions. The residue was then dried in an oven at 353 K for 24h.

Acidity Measurement

10 g of clay was added to 100 mL of distilled water. The mixture was stirred vigorously. The pH of the clay suspension was then measured via pH meter.

In the acidity test, 10 g of clay was boiled for 3 min with 10 mL distilled water then filtered and washed with another 100 mL of distilled water. The combined filtrate and wash liquid were then titrated with 0.1 N NaOH solutions to phenolphthalein end point. The acidity was then calculated as percentage weight of NaOH per gram of clay

$$\text{Acidity} = \frac{V * N * 40}{W_c} * 100 \quad (1)$$

where V is the volume of sodium hydroxide used in titration (mL), N is normality of sodium hydroxide and W is weight of clay (g).

Batch Adsorption Study

Batch adsorption isotherm experiments were conducted by varying concentrations of Cr (VI) from 50 mg/L to 500 mg/L, at constant adsorbent dose 500 mg. While adsorbent dosage was varied from 100 mg to 500 mg at constant concentration of Cr (VI) of 50 mg/L. The effects of time, temperature and pH were

studied with Cr (VI) concentration of 100 mg/L and an adsorbent dosage of 500 mg. The concentration of free Cr (VI) ions in the effluent was determined with 1, 5-diphenyl carbazide (DPC) in acidic solution spectrophotometrically (Elico SL 171) at λ max 535 nm. Adsorption isotherm study was done with 100 mg/L Cr (VI) at 333 K at pH 3 and time of contact was maintained at 200 min. The agitation was done at 240 rpm in the Erlenmeyer flasks on an orbital shaker. For the thermodynamic study, temperature was varied from 303 to 333 K.

The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = \frac{V(c_0 - c_e)}{M} \quad (2)$$

where c_0 and c_e (mg/l) are the liquid-phase concentrations of Cr (VI) at initial and equilibrium, respectively, V (L) is the volume of the solution and M (g) is the mass of dry prepared sorbent used. The percent removal efficiency of chromium ion by the acid activated bentonite was calculated as:

$$Y(\%) = 100 \frac{c_0 - c_i}{c_0} \quad (3)$$

where c_0 and c_i are the initial and final concentration of the chromium solution.

Results and Discussions

Characterization of the Modified Bentonite Sorbent

The chemical compositions of the bentonite after acid activation are shown in Table-1. The removal of the di-octahedral cations depends on their form and amount within the bentonite sample. They are present in small quantity as exchangeable cations. It was observed that Ca²⁺ was easily removed more than the others of Na⁺ and K⁺. The Calcium ion occurred as calcite which dissolves easily in acid medium, while the Na and K ions were present as feldspars that are resistant to acid attack. The removal of the tri-octahedral cations of Al³⁺, Fe³⁺, and Mg²⁺, was observed to be dependent on the intensity of the acid attack, their removal increased as the acid concentration was increased until 6mol/l, and thereafter their removal decreased as the concentration increased to 10mol/l. As can be observed from the table, the octahedral cations Al³⁺, Fe³⁺, and Mg²⁺, reduced appreciably as the intensity of the acid treatment increased, while the tetrahedral cation, like Si⁴⁺, increased with severity of acid

treatment. The behaviour shown by the Al_2O_3 , Fe_2O_3 , and MgO content with progressive acid treatment is related to the progressive dissolution of the clay minerals. The octahedral sheet destruction passes the cations into the solution, while the silica generated by the tetrahedral sheet remains in the solids, due to its insolubility. Pesquera et al [17] suggests that this free silica generated by the initial destruction of the tetrahedral sheet is polymerized by the effect of such high acid concentrations and is deposited on the undestroyed silicate fractions, protecting it from further attack. The Mg^{2+} was easily removed at mild treatment of the acid reaching 85.9% at 4mol/l for 20 hours. The removal of Al^{3+} and Fe^{3+} were both slow with Fe^{3+} having faster removal rate at the same treatment. This is in agreement with the findings of other authors [14].

Surface Area and Cation Exchange Capacity of the Bentonite Sorbent

Apart from leaching out of the octahedral and tetrahedral cations, the acid activated samples showed a decrease in the cation exchange capacity and increase in the surface area with increase in the severity of acid treatment as shown in Table-1, but this was observed to reverse for higher acid concentration. The increase in the surface area from

the natural to acid activated samples could be related to the elimination of the exchangeable cations, delamination of smectite and the generation of microporosity during the process. The decrease observed for higher acid concentration could be explained by the passivation of the clay from further acid attack by the insoluble silica.

The cation exchange capacity (CEC) data also given in Table-1 showed that there is a sharp decrease in the CEC of 47.6% from sample NK0 to NK6. Smectite sample NK8 maintained only 48.2% of the initial CEC, while sample NK10 possessed only 34.5% of the initial CEC. This progressive decrease in CEC values upon treatment with hydrochloric acid can be understood in terms of the depopulation of octahedral sheet. It is well established that leaching of the octahedral cations (Mg^{2+} , Fe^{2+} , Al^{3+}) results in a reduction of the negative layer charge and therefore of the CEC. The net reduction in CaO content indicated that the Ca^{2+} exchange cations were replaced by hydrogen ions and/or polyvalent cations leached from the octahedral sheet. The decrease in the octahedral sheet oxides (Al_2O_3 , MgO and Fe_2O_3) along with the concomitant increase in silica content proved that the original structure was altered.

Table-1: X-ray fluorescence analysis of the modified samples: Percentage of cations remaining after different acid treatments, in relation to their content in the untreated bentonite, expressed in oxide form.

Acid concentration (mol/L)	Time (h)	Chemical composition (%)							Acidity	Surface area (m^2/g)	Cation exchange capacity (meq/100g)
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	CaO	K ₂ O			
Raw bentonite	0	52.8	25.7	10.4	5.5	2.1	0.9	0.5	0.01	37.6	104
2	2	53.2	24.4	9.7	5.1	2.1	0.8	0.5	0.10	43.8	84
	4	54.7	23.6	8.9	4.6	2.1	0.7	0.5			
	8	55.3	22.1	8.1	3.9	1.9	0.6	0.5			
	12	56.4	20.3	7.5	3.5	1.9	0.5	0.5			
	16	57.5	18.9	7.1	3.0	1.8	0.4	0.5			
4	2	55.2	22.2	7.7	4.3	2.0	0.7	0.5	0.30	59.5	75
	4	57.5	20.1	6.2	3.4	2.0	0.6	0.5			
	8	58.5	18.6	5.7	2.5	1.8	0.5	0.4			
	12	59.9	15.4	5.0	1.9	1.7	0.4	0.4			
	16	60.7	13.7	4.6	1.2	1.6	0.3	0.4			
6	2	62.8	11.3	4.1	0.9	1.5	0.2	0.3	0.50	74.1	54
	4	58.7	18.5	6.3	3.7	1.9	0.5	0.4			
	8	60.8	15.6	4.9	2.8	1.7	0.4	0.4			
	12	63.2	12.2	3.4	2.0	1.6	0.3	0.4			
	16	66.3	9.7	2.4	1.4	1.5	0.2	0.3			
8	2	69.2	5.8	1.8	0.8	1.4	0.1	0.3	0.55	66.3	45
	4	72.8	2.5	0.7	0.4	1.3	0.01	0.3			
	8	59.1	18.7	6.5	3.0	1.7	0.4	0.4			
	12	61.1	16.1	5.8	2.4	1.6	0.3	0.4			
	16	63.9	12.8	4.0	1.7	1.5	0.3	0.3			
10	2	66.7	10.5	2.7	1.0	1.4	0.2	0.3	0.60	62.4	33
	4	69.8	6.4	2.1	0.7	1.3	0.1	0.2			
	8	73.1	3.7	1.4	0.4	1.1	0.01	0.2			
	12	59.7	19.1	6.9	2.9	1.5	0.4	0.3			
	16	61.5	16.9	6.2	2.2	1.3	0.2	0.3			
20	8	64.3	13.3	4.6	1.6	1.2	0.1	0.2	0.60	62.4	33
	12	66.9	11.1	3.2	0.9	1.0	0.01	0.2			
	16	70.2	7.2	2.8	0.6	0.9	0.01	0.1			
20	73.2	4.3	1.9	0.3	0.8	0.01	0.1				

Table-2: Effect of initial concentration of Cr (VI) on amount adsorbed, mg/g of Cr (VI) and removal, % on activated Nkaliki bentonite (Time 200 min, pH 3, Temperature 333 K, Adsorbent dosage 500 mg, and Agitation speed 240 rpm).

Initial conc. of Cr (VI), C_0 (mg/L)	Liquid-phase conc. of Cr (VI), C_e (mg/L)	Amount adsorbed at equil., q_e (mg/g)	Cr (VI) Removed, %
50	0.49	4.95	99.02
100	2.76	9.72	97.24
150	9.61	14.04	93.59
200	19.72	18.03	90.14
250	38.61	21.14	84.56
300	60.42	23.96	79.86
350	93.61	25.64	73.25
400	128.93	27.11	67.77
450	163.52	28.65	63.66
500	211.56	28.84	57.69

Table-3: Effect of contact time on the Cr (VI) removal by activated bentonite (initial concentration, 100mg/L; pH, 3; agitation speed, 240 rpm; adsorbent dosage, 500mg; temperature, 333K).

Time, min	Liquid-phase conc. of Cr (VI), c_t (mg/L)	Amount adsorbed at time t , q_t (mg/g)	Cr (VI) Removed, %
20	68.28	3.17	31.72
40	60.42	3.96	39.58
60	52.83	4.72	47.17
80	46.34	5.37	53.66
100	33.54	6.65	66.46
120	21.47	7.85	78.53
140	14.26	8.57	85.74
160	6.80	9.32	93.20
180	2.12	9.79	97.88
200	1.84	9.82	98.16
220	1.64	9.84	98.36
240	1.32	9.87	98.68

Acidity of the Modified Samples

The acidity of the activated smectites samples was affected by the acid activation process. The acidity of the bentonite samples is presented in Table-1. The acidity was observed to increase with an increase in the severity of the acid treatment. In fact, it has been observed that the number of acid centers significantly increases in acid activated clay samples compared with natural samples. Kumar et al., [18] reported that Bronsted acid sites are generated by exchange of inter-lamellar cations with protons and Lewis acid sites correspond to Mg^{2+} and Al^{3+} present at the edges of octahedral sheets. The Bronsted acidity stems from terminal hydroxyl groups and from bridging oxygen. An enhancement on the acidity of the host matrix following acid treatment has been observed [19] and explained as the number of the matrix protons (on the clay sheets) not associated with the interlayer cations, which may be increased by acid treatment.

Effect of Process Variables

Initial Metal Ion Concentration

The effect of the initial chromium ion on the adsorption performance of the acid activated bentonite was studied at an initial concentration range of 50mg/L to 500mg/L, while other variables were kept constant at pH of 3, adsorbent dosage of 500mg, stirring speed of 240 rpm, and temperature of 333 K.

The results of the experimental data are shown in Table-2. The percentage removal of Cr (VI) reached 98.9% at initial concentration of 50mg/L. The amount adsorbed was increased with increase in concentration of adsorbate. The percentage removal of Cr (VI) decreases with an increase in initial Cr (VI) concentration. It may be due to an increase in the number of Cr (VI) ions for the fixed amount of activated bentonite. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake. Uptake of the Cr (VI) also increased with increasing the initial metal concentration tending to saturation at higher metal concentrations [20].

Effect of Time

To study the effect of time on the adsorption of Cr (VI) onto activated bentonite, the time was varied from 20 min to 240 min while keeping other variables at constant values. The results of the experimental data are shown in Table-3. Adsorption started at 20 min with 31.72% and reached up to 98.16% from 200 min and the quantity adsorbed was 9.82 mg/g. There was no significant change in adsorption of Cr (VI) after 200 min. Further studies made after 200 min up to 240 min showed no significant increase in the adsorption rate. The initial rapid rate of adsorption was may be due to the availability of the positively charged surface of the adsorbent for anionic Cr (VI) species present in the

solution. The later slow adsorption rate was may be due to the electrostatic hindrance caused by already adsorbed negatively charged adsorbate species and the slow pore diffusion of the ions [21].

Effect of Adsorbent Dosage

The experiments were carried out under the conditions described earlier and varying adsorbent dosage from 100 mg to 500 mg. The effect of adsorbent dose on the adsorption of chromium by activated bentonite is presented in Fig. 1. The Cr (VI) removal efficiency increases with increase in adsorbent dose, since contact surface of adsorbent particles increased and it would be more probable for HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions to be adsorbed on adsorption sites [22]. Maximum adsorption was observed at 500 mg i.e. 98.05%. It can be observed that removal efficiency of the adsorbents generally increased with increasing the quantity. It is due to the availability of exchangeable sites for the adsorbate [23].

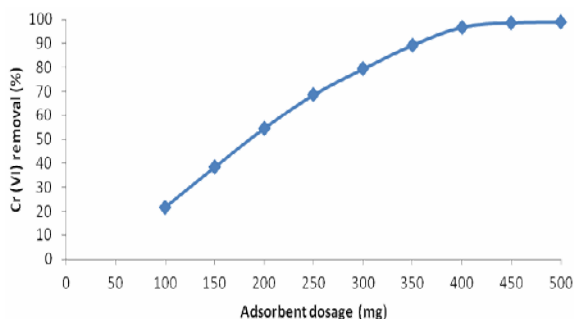


Fig. 1: Effect of adsorbent dosage on the Cr (VI) removal on to activated bentonite (initial conc. 50mg/L, pH 3, contact time 200 min, and stirring speed 300 rpm).

Effect of pH

The effect of pH on the adsorption of Cr (VI) on to activated Nkaliki bentonite was studied in the range of 1 to 9 with an initial concentration of 100 mg/L. The experimental results are shown in Fig. 2. Maximum adsorption of Cr (VI) was observed at the acidic pH of 3 with percentage removal up to 98.76. This is because at lower pH there is increase in H^+ ions on the carbon surface, and the presence of HCrO_4^- ions resulting in significant strong electrostatic attraction. As the pH increases there was exponential decrease in the Cr (VI) adsorption and at pH values greater than 6.0 there was no significant adsorption. This was due to dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates.

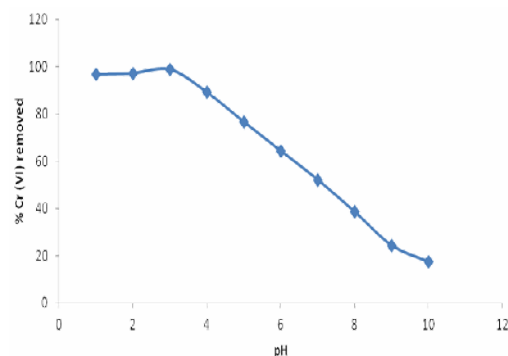
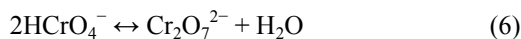
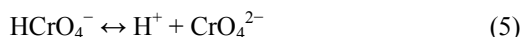
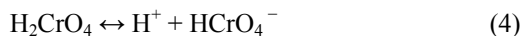


Fig. 2: Effect of pH on the % Cr (VI) adsorbed on to activated Nkaliki bentonite.

At pH 1.0, the chromium ions exist in the form of H_2CrO_4 , while in the pH range of 1– 6 different forms of chromium ions such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ coexist of which HCrO_4^- predominates. As pH increases this form shifts to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system [24].

Adsorption Isotherm

Adsorption isotherms, which are the presentations of the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature were studied. The mechanism of adsorption could be determined by evaluating the equilibrium data also known as adsorption data obtained from the experiments. In this present study, Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were used to examine the adsorption data.

Langmuir Isotherm

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent and that the formation of monolayer takes place on the surface of the adsorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The Langmuir isotherm model is given by the following equation:

Table-4: Langmuir, Freundlich, and Dubinin-Radushkevich isotherm parameters for adsorption of Cr (VI) on to activated Nkaliki bentonite

Langmuir isotherm				Freundlich isotherm			Dubinin-Radushkevich isotherm			
q_m (mg/g)	K_L (L/mg)	R_L	R^2	K_f (mg/g)	N	R^2	X_m (mg/g)	$\beta(10^{-9})$	E (kJ/mol)	R^2
30.30	0.094	0.0479 to 0.9552	0.9964	6.902	3.472	0.9803	8.82	6	-9.128	0.7866

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (7)$$

where, C_e is the equilibrium concentration (mg/L); q_e is the amount of metal ion adsorbed (mg/g); q_m is the Langmuir constant for adsorption capacity (mg/g); K_L is sorption equilibrium constant (L/g).

The values of q_m and K_L were evaluated from the slope and intercept of the plot of C_e/q_e versus C_e as shown in Fig. 3 [25] and are given in Table-4.

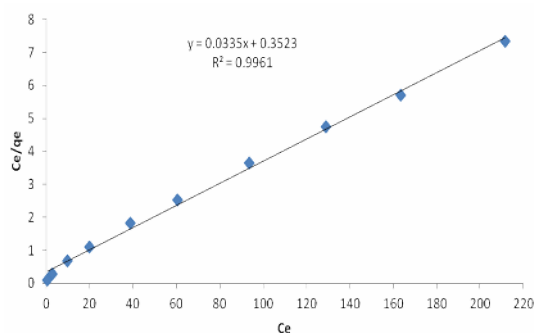


Fig. 3: Langmuir plot for Cr (VI) adsorption on to activated Nkaliki bentonite.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [26] also known as the separation factor, given by

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (8)$$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$. Results of R_L calculated from this study (Table-4) lies between 0.0479 and 0.9560 and this is consistent with the requirement for favorable adsorption of Cr (VI) on to activated Nkaliki bentonite.

Freundlich Isotherm

Freundlich isotherm assumes that the uptakes of metal ions occur on a heterogeneous

surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. It is a most popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium [27]. The Freundlich equation is expressed as

$$q_e = K_f C_e^{\frac{1}{n}} \quad (9)$$

where, K_f is the measure of adsorption capacity and n is the adsorption intensity. Linear form of Freundlich equation [28] is,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (10)$$

where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L) and K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. A plot of $\log q_e$ vs $\log C_e$ gives a linear trace with a slope of $1/n$ and intercept of $\log K_f$ and the results are also given in Table-4. When $1/n > 1.0$, the change in adsorbed metal ion concentration is greater than the change in the metal ion concentration in solution.

Dubinin-Radushkevich isotherm

The D-R equation has been widely used to explain energetic heterogeneity of solid at low coverage as monolayer regions in micro-pores. The equation is given by

$$\ln q_e = \ln X_m - \beta \epsilon^2 \quad (11)$$

where β is the activity coefficient related to mean adsorption energy, X_m the maximum of adsorption capacity and ϵ is the Polangi potential, which is equal to

$$\epsilon = RT \ln \left(\frac{1}{C_e} \right) \quad (12)$$

where R and T are the gas constant (kJ/mol/K) and temperature (K), respectively.

The adsorption energy E expressed as;

$$E = - \frac{1}{(-2\beta)^{0.5}} \quad (13)$$

Table-5: Parameters of the Pseudo-first-order, Pseudo-second-order, Elovich, and Intra-particle kinetic models together with their regression coefficients.

Pseudo-first-order			Pseudo-second-order			Elovich			Intra-particle diffusion		
q_e (mg/g)	k_1 (g/mg min)	R^2	q_e (mg/g)	$k_2 \times 10^{-4}$ (g/mg min)	R^2	A (g/mg min)	B (mg/g)	R^2	k_{id} (mg/g min)	C_i	R^2
28.91	0.0276	0.8906	14.93	6.138	0.9958	0.3022	0.309	0.9321	0.71	-0.332	0.9602

Reveals the nature of adsorption. If the value of adsorption energy E ranged between -1 and -8 kJ/mol, adsorption process is physical, and if the value of E ranged between -9 and -16 kJ/mol, it is chemical adsorption. The parameters of the D-R equation were calculated from the slope and intercept of the linear plot of $\ln q_e$ versus ε^2 and are given in Table-4.

The adsorption energy E value obtained - 9.13 kJ/mol showed that the adsorption of Cr (VI) on to activated Nkaliki bentonite is a chemical process.

The good fit of the experimental data and the determination coefficient closer to unity indicated the applicability of the Langmuir isotherm model to describe the adsorption of Cr (VI) on to activated Nkaliki bentonite.

Adsorption Kinetics

The effect of contact time on the adsorption of Cr (VI) on activated Nkaliki bentonite was studied and the results show that adsorption increased with increase in contact time. The experimental data were examined by pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic equations to understand the dynamics and mechanism of the adsorption process. A simple pseudo-first order equation was used and it is given by

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (14)$$

where, q_e and q_t are the amount of Cr (VI) adsorbed at equilibrium and at time t (min) respectively, and k_1 is the rate constant of the pseudo-first order adsorption process [29]. The linear form of the equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (15)$$

The values of k_1 and q_e were calculated from the slope and intercept of the linear plot of $\log (q_e - q_t)$ versus t and are given in Table-5.

The corresponding pseudo-second order rate equation is given as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (16)$$

where, k_2 is the rate constant for the pseudo-second order adsorption process ($\text{g mg}^{-1} \text{min}^{-1}$). The slope and intercept of the plot of t/q_t versus t (Fig. 4) were used to calculate the values of q_e and k_2 as presented in Table-5. The value of the regression coefficient calculated from the plot of the second-order kinetic plot shows that it best fitted the experimental data and can be used to describe the adsorption of Cr (VI) on to activated Nkaliki bentonite.

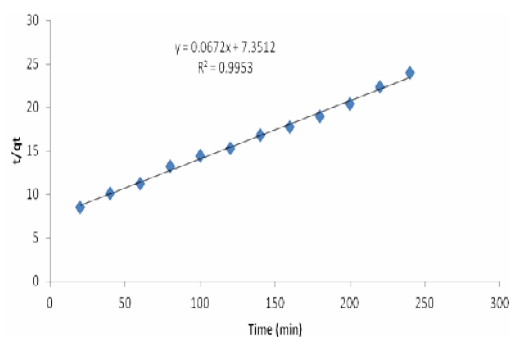


Fig. 4: Pseudo-second-order kinetic plot for Cr (VI) adsorption on to activated Nkaliki bentonite.

The Elovich model is presented by the following equation:

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (17)$$

where α is the initial adsorption rate (mg/g/min) and β is the desorption constant (g/mg). The slope and intercept of the plot of q_t versus $\ln t$ were used to calculate the values of the constants α and β as shown in Table-5. The value of the determination coefficient obtained from the linear plot of Elovich (Table-5) models are not high ($R^2 < 0.9321$), suggesting that the applicability of this model to describe the adsorption process of Cr (VI) on to activated Nkaliki bentonite is not feasible.

Intra-Particle Diffusion Study

The adsorption mechanism of adsorbate on to adsorbent follows three steps: (1) transport of adsorbate from the boundary film to the external

surface of the adsorbate; (2) adsorption at a site on the surface; (3) intra-particle diffusion of the adsorbate molecules to an adsorption site by a pore diffusion process. The slowest of the three steps controls the overall rate of the process. The possibility of intra-particle diffusion was explored by using an intra-particle diffusion model. The intra-particle diffusion varies with square root of time and is given as,

$$q_t = k_{id}t^{1/2} + C_i \quad (18)$$

where, q_t is the amount adsorbed at time t , $t^{1/2}$ is the square root of the time, k_{id} is the intra-particle diffusion rate constant (mg/g min^{1/2}), and C_i is the intercept at stage i and is related to the thickness of the boundary layer. Large C_i represents the greater effect of the boundary layer on molecule diffusion. The intra-particle diffusion rate constant was determined from the slope of the linear gradients of the plot q_t versus $t^{1/2}$ and their values are presented in Table-5. The intra-particle diffusion process is controlled by the diffusion of ions within the adsorbent.

The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. Initially the concentration gradient between the film and the solid surface is large, and hence the transfer of solute onto the solid surface is faster. As time increases, intra-particle diffusion becomes predominant. Hence solute takes more time to transfer from solid surface to internal adsorption sites through the pores.

Adsorption Thermodynamics

The thermodynamics of an adsorption process is obtained from a study of the influence of temperature on the process. Temperature effect has been studied for the adsorption of Cr (VI) ions by activated Nkaliki bentonite. It has been found that the adsorption capacity increased from 5.52 mg/g to 9.87 mg/g as the temperature was increased from 303 K to 333 K at Cr (VI) ion concentration of 100 mg/L, pH 3.0 and the other conditions were kept constant. This indicates that the adsorption reaction was endothermic in nature. The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbate and adsorbent, creation of some new adsorption sites or the increased rate of intra-particle diffusion of Cr (VI) ions into the pores of the adsorbent at higher temperatures.

The standard Gibb's energy was,

$$\Delta G^\circ = -RT \ln K_c \quad (19)$$

K_c represents the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate within the solution. The values of K_c can be deduced from the relationship,

$$K_c = \frac{q_e}{C_e} \quad (20)$$

where, q_e is the amount adsorbed on solid phase at equilibrium and C_e is the equilibrium concentration of metal ion in the solution. Other thermodynamic parameters such as change in standard enthalpy (ΔH°) and standard entropy (ΔS°) were determined using the Van't Hoff's equation

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (21)$$

The values of ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff's plot of $\ln k_c$ versus $1/T$ (Fig. 5), positive value of ΔH° indicates that the adsorption process is endothermic. The negative values of ΔG° reflect the feasibility of the process and the values become more negative with increase in temperature. Standard entropy determines the disorderliness of the adsorption at solid-liquid interface. Thermodynamic parameters are summarized in Table-6. The positive value of ΔS° shows increasing randomness at the solid/liquid interface during the adsorption of Cr (VI) ions on activated bentonite.

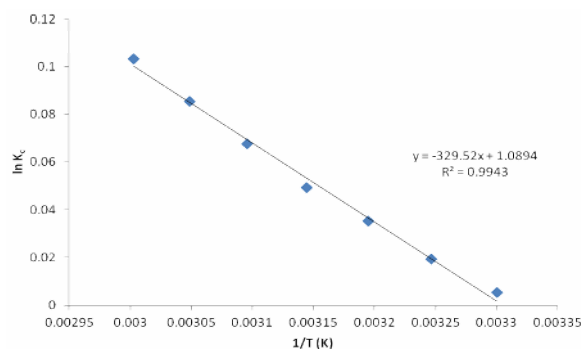


Fig. 5: Plot of $\ln k_c$ versus $1/T$ for Cr (VI) adsorption on to Nkaliki activated bentonite.

Table-6: Thermodynamic parameters of adsorption of Cr (VI) on to activated bentonite.

Temperature, K	ΔG° , kJ/mol	ΔH° , kJ/mol	ΔS° , J/mol K
303	-0.013		
308	-0.049		
313	-0.091		
318	-0.13	2.739	9.052
323	-0.181		
328	-0.232		
333	-0.285		

Conclusions

The acid activation of Nkaliki bentonite has successfully been studied and results of the activation show that the physico-chemical properties of the bentonite were improved. Such properties include; surface area, cation exchange capacity, acidity, and sorption performance. The activated bentonite was used to successfully adsorb Cr (VI) from aqueous solution. The removal of Cr (VI) ions with an initial concentration of 50mg/g was found to be 99.02% after shaking for 200 min at constant temperature of 333 K. The experimental data for the adsorption process were well fitted to the Langmuir adsorption isotherm model relative to the fit of Freundlich and Dubinin-Radushkevich models. The kinetic analysis showed that adsorption of Cr (VI) ions obeyed the pseudo-second-order kinetic equation. The increase in the adsorption capacity observed with increasing temperature showed that the adsorption process was chemical in nature, spontaneous and endothermic as confirmed by the evaluation of the relevant thermodynamic parameters, viz. ΔG° , ΔH° , and ΔS° . Results from this study has shown that Nkaliki bentonite can be used as a low-cost, readily available, and easily prepared sorbent for the effective removal of Cr (VI) from aqueous solution.

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