Chromium and nickel metal ions removal from contaminated water using Nigerian bentonite clay

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Abstract

In this work, bentonite clay was characterized and investigated for the adsorption of chromium and nickel metal ions from aqueous solution. The clay, calcined at 650 °C, was characterized for physical, chemical and textural properties. Nickel sulphate hexahydrate ($NiSO_4.6H_2O$) and chromium tri oxide (Cr_2O_3) solutions were used as metal model compounds to evaluate the adsorption efficiency of the clay in a batch mode. The initial metal ions concentration ranged from 10 to 50 mg/L and the maximum removal efficiency was 99.40% for Cr (III) and 71.50% for Ni (II) metal ions. Langmuir and Freundlich models were utilized for the analysis of the adsorption equilibrium isotherm. The experimental data fitted well into the Freundlich model for Cr (III) with a regression coefficient (R^2) of 0.996 and the Langmuir model for Ni (II) having an R^2 value 0.994. The pseudo-second order kinetic model fitted well for both chromium and nickel and their adsorption from single metal solutions followed the order Cr > Ni.

Key words: adsorption, bentonite clay, chromium, isotherms, kinetics, nickel

Highlight

- The local clay has not been reported in any scholarly journal or publication. The removal of nickel and chromium using this clay has been found to be effective. The data obtained will form a baseline for references and learning purposes.

INTRODUCTION

Contamination of aquatic systems is a serious environmental issue and therefore the development of an efficient and suitable technology to remove heavy metals from aqueous solutions is necessary. Different toxic organic and inorganic pollutants such as solvents, spilled oil, polyaromatic hydrocarbons (PAHs), dyes, metal and metalloid species, and so on, have been found at basic levels in waste water, ground and surface waters (Pandey & Ramontja 2016a).

Metal ions such as mercury, cadmium, chromium, nickel, palladium, and so on are introduced in the environment through natural sources such as weathering and erosion of rocks, and anthropogenic sources such as chemical manufacturing plants, and electroplating, battery, pesticide and fertilizer industries. Even at very low concentrations, these metal ions tend to accumulate in living organisms, causing different health disorders in humans and animals depending on the exposure rate and dosage

(Pandey & Tiwari 2015; Pandey & Ramontja 2016b; Adewoye *et al.* 2017). According to WHO, the maximum permissible limit of nickel and chromium in drinking water is 6 μg/L and 50 μg/L respectively (Dogara *et al.* 2017).

The common oxidation states of chromium are from +2 to +6; however, only two oxidation states, +3 and +6, are of environmental significance and the hexavalent form is 500 times more toxic than the trivalent. Human toxicity of chromium includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage (Mansri *et al.* 2009). Health problems associated with inhaling nickel dust are diarrhoea, renal oedema, nausea, chest pain, pulmonary fibrosis and gastrointestinal ache (Ugwu & Igbokwe 2019).

Due to the toxic effect of these heavy metals, there is need for their removal from industrial wastewaters. Many techniques for heavy metal removal from contaminated water include ion exchange, solvent extraction, foam flotation, coagulation, chemical precipitation, membrane separation, reverse osmosis, electrolysis and adsorption. Among these methods, adsorption has been found to be superior to the other techniques, due to its low cost, flexibility, simplicity and ease of operation, robustness, insensitivity to toxic pollutants, high removal efficiency and environmental compatibility (Akpomie & Dawudo 2015; Naser *et al.* 2019; Pandey *et al.* 2020a), and the adsorbents can be regenerated by suitable desorption processes for re-use (Pandey *et al.* 2020b).

Bentonite clay is a layered phyllosilicate that acts as a natural scavenger of pollutants. It is easily available all over the world and has a porous structure classified into macro pores, mesopores and micropores. The adsorption capacity depends on the presence of micro and mesopores (Pandey & Ramontja 2016c; Pandey 2017). However, changing the structure of bentonite through acid and thermal activation, treatment with cationic surfactants, calcination, and so on is required for improving its applicability for the adsorption process (Prathiksha & Balakrishna 2018). Modified bentonite-based composites offer a good alternative for use as adsorbents in wastewater remediation applications. Inorganic/organic nanocomposites possess properties of both organics and inorganics such as good permeability, selectivity, mechanical strength, and thermal and chemical stability (Pandey & Mishra 2011). Polymer/silica nanocomposites have been employed in a variety of applications including adsorption processes.

Activated carbon is regarded as the most effective adsorbent for heavy metals. However, due to its high cost, and the difficulty and expenses involved in regeneration, clays such as bentonite are being considered as alternative low-cost adsorbents. Several works have presented on the use of bentonite as adsorbents for cationic contaminants, including heavy metal ions, cationic dyes, and so forth.

Bentonite clay exists in many parts of the world and these deposits have different properties due to their different geological locations. The application of Dijah-Monkin bentonite as a local content in the adsorption process has not been reported by researchers. Hence, this is one of the major reasons for the present work that can be novel in this field.

The aim of this research is to evaluate the adsorption potential of Dijah-Monkin bentonite clay for chromium and nickel ion removal from a contaminated aqueous medium. Nigeria has a huge deposit of bentonite clay, yet the resources are underutilized as their suitability and potentials have not been fully investigated. Waste solutions containing heavy metals need treatment for their removal due to the health risk posed to humans and living creatures. The experiment was performed at different initial metal ion concentrations, contact times and temperature regimes. Isotherm and kinetic models were developed and tested to appropriately describe the experimental data.

MATERIALS AND METHODS

Sample purification and modification

The raw bentonite clay sample was obtained from the mining site at Dijah-Monkin, Taraba State, North-East Nigeria (8°00′N latitude 10°30′E longitude). The sample was first purified by beneficiation

and followed by modification using calcinations. Beneficiation is the treatment of raw material to improve its physical or chemical properties by removing impurities, which results in a higher-grade product.

Beneficiation of bentonite

The beneficiation of bentonite was carried out according to the methods adopted by Ahmed *et al.* (2012) and Nwafulugo *et al.* (2014). 10 kg of raw bentonite clay was weighed and crushed down from lumps to coarse powder form using a wooden mortar and pestle. The coarse powder was soaked in 90 litres of water in a plastic container and the mixture was allowed to stay for 24 hours. It was then plunged (stirred) for 3 hours at room temperature. The stirred mixture was then allowed to remain in the container for 24 hours and then plunged for another 3 hours. The stirred mixture was then allowed to remain in the container for 24 hours for the coarse quartz impurities to sediment to the bottom, leaving a colloidal solution of bentonite at the top. The colloid bentonite was collected and separated from the quartz sediments and sieved through a 230 mesh Tyler sieve (63 μm sieve opening) to further remove coarse impurities. The clay obtained was allowed to settle and thicken for 5 days in a plastic container. The thickened clay was put in a filter cloth and pressed under a hydraulic press to squeeze out the water. The resulting cake was dried in an oven at 120 °C to constant weight, broken down to powder and stored in a large polyethylene bag for the subsequent experiments.

Calcination of bentonite clay

20 g of the beneficiated clay was fired gradually in an electric furnace to 650 °C and soaked at that temperature for 3 hours. The calcination temperature was selected based on the fact that the hydroxyl group (chemically combined water or water of hydration) in montmorillonites' structure gets destroyed at temperatures between 600 °C and 750 °C (Ahmed *et al.* 2012). The calcined clay was allowed to cool down in desiccators and characterized prior to its application as an adsorbent.

Sample characterization

The bentonite clay was characterized for chemical composition, loss on ignition (LOI), bulk density, micro porosity, SEM and TGA. The micro porosity was evaluated from the BET Thermo Scientific (Surfer machine), USA and scanning electron microscopy (SEM) was determined using a field emission scanning electron microscope model SU8020 (Hitachi, Japan). The thermogravimetric analysis (TGA) curve was obtained using Q500 equipment (TA Instruments, USA). Some physicochemical characteristics of the bentonite clay have been reported elsewhere (Jock *et al.* 2016).

Preparation of stock solution

The solutions of Cr (III) and Ni (II) metal ions were prepared from analytical grade nickel sulphate hexahydrate ($NiSO_4.6H_2O$) and chromium trioxide (Cr_2O_3). Stock solutions of 1,000 mg/L concentrations for Cr (III) and Ni (II) metal ions were prepared by dissolving CrO_3 and $NiSO_4.6H_2O$ in 1 L of distilled water respectively. Thereafter, the stock solutions were further diluted to obtain working solutions of the desired initial concentrations.

Adsorption experiments

The adsorption process was carried out in a batch reactor by varying metal ion concentration and contact time for isotherm and kinetic studies respectively. For the effect of initial concentration, standard

metal solutions ranging from 10 to 40 mg/L were prepared by diluting the stock solutions. 0.5 g of the calcined clay was mixed with 25 mL of the metal solution in 150 mL Erlenmeyer flasks. The mixture was shaken at 200 rpm stirring rate and 25 °C for 30 minutes. The suspension was filtered and the residual concentrations of heavy metals were analyzed using an atomic absorption spectrometer (AAS) (Shimadzu, AA-6880 Series, Japan).

For the effect of time, 50 mg/L solutions of nickel and chromium metal ions were used. 25 mL of each solution was added in a 150 mL flask containing 0.5 g of the clay sample. Flasks were kept in a shaker at various contact times (15–60 min) and constant speed of 200 rpm and 25 °C. After each time, the mixture was filtered and the metal concentration remaining in the supernatant was analyzed by an atomic absorption spectrometer (AAS).

RESULTS AND DISCUSSION

Characteristics of bentonite adsorbent

The chemical analysis of the clay in Table 1 shows that the clay consists mainly of silica (51.7%) and alumina (18.0%) as well high iron (14.47%) content. The elemental composition shows the presence of K and Ag in minor quantity while Ti and Mn are in trace amounts. The most abundant component of Si and Al in the sample confirmed the basic elements of the smectite clay group (Araujo *et al.* 2013). The high iron content explained the brownish and reddish appearance of bentonite clay. The clay can be designated as polycationic bentonite due to the presence of Ca^{2+} and K^+ cations, which are normally exchangeable with positively charged pollutants (Bertagnolli *et al.* 2011). The pH value suggests that the bentonite clay is slightly acidic. The low LOI obtained in the clay indicates greater loss on ignition took place during calcination at 650 °C. This is largely due to the expulsion of structural hydroxyl water and volatile organic components such as CO_2 and SO_2 in the clay (Saika & Parthasarathy 2010). The density value of the bentonite sample is within the range of 1.1–1.4 g/cm^3 for pure clay and other fine-textured soil minerals (Kukwa *et al.* 2014). Microporosity of the calcined clay, which might have been increased on calcination due to the liberation of hydroxyl group at elevated temperature, creating a path for the pore volume, is expected to enhance the adsorption process (Zhu *et al.* 2016).

**Table 1** | Physiochemical properties of calcined bentonite

Component (%)								Parameters			
Al	Si	K	Ca	Fe	Ti	Ag	Mn	LOI (%)	P^H	Density (g/cm^3)	Microporosity (%)
18.0	51.7	8.11	1.93	14.47	1.86	3.15	0.24	0.09	6.0	1.15	83

The micrograph of the raw bentonite reported elsewhere (Jock *et al.* 2016) showed that the bentonite grains are an aggregated mass of irregularly shaped particles that appeared to have been formed by several flaky particles stacked together in the form of agglomerates, while the micrograph of the calcined clay shown in Figure 1 is of leaf-like type with no defined particle format. The irregular shape particles depict the adsorptive characteristic of the clay. Generally, bentonite clay (montmorillonite) exhibits ultrafine, thin, leaf-like crystals forming a dense aggregate, or open honeycomb texture (Zuzana *et al.* 2012).

Figure 2 shows the thermograph of the clay sample. The first weight loss is related to removal of water molecules and associated cations from the clay gallery during thermal treatment. The second thermal transition of the crystal water removal collapsed with the thermal degradation of the clay, which was already calcined at 650 °C. This weight loss (1.5%) could also be attributed to the
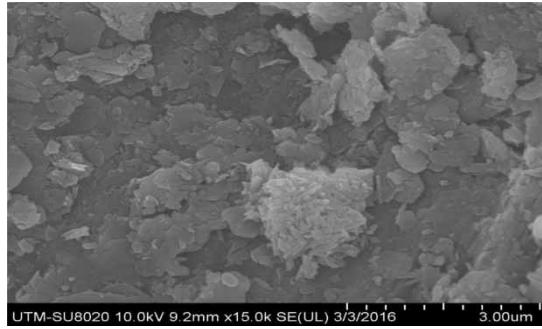
Figure 1 | Scanning electron micrograph for calcined bentonite sample.
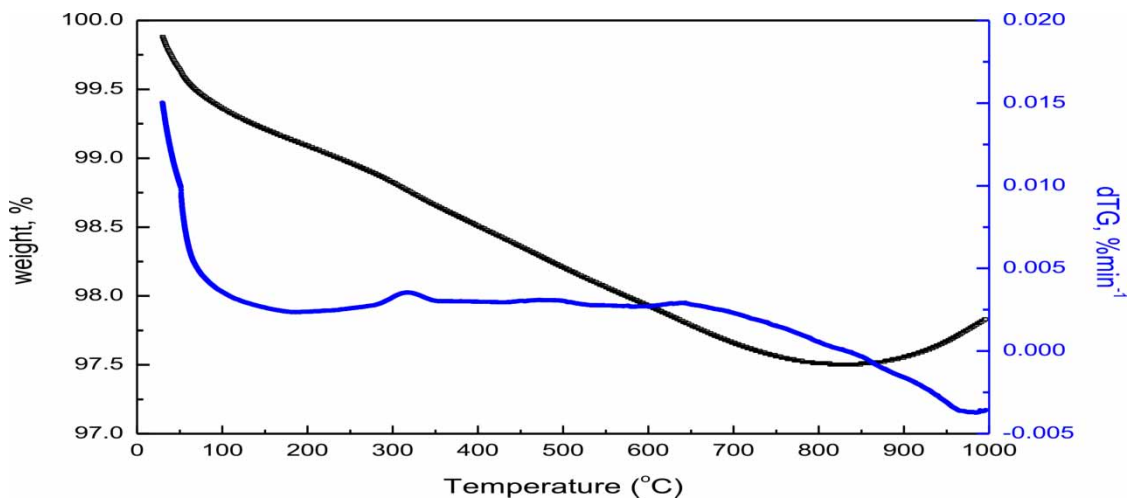
Figure 2 | Thermogram of calcined bentonite sample.

decomposition of the clay structure. The low weight loss in the temperature range of the dehydration step implied the change in thermal stability of the modified bentonite (Hassan 2005).

Adsorptive characteristics of bentonite clay

Effect of initial concentration

The effect of the initial concentration on percentage removal of Cr (III) and Ni (II) ions is calculated by Equation (1).

$$\%Ads = \frac{C_i - C_f}{C_i} \tag{1}$$

where, $\%Ads$ is the amount of metal ions removed, C_i and C_f are the initial and final concentrations (mg/L) of the metal ions respectively.

The initial concentrations for Cr (III) and Ni (II) were varied from 10, 20, 30 to 40 mg/L using an adsorbent amount of 0.5 g and contact time of 30 min. The removal efficiency slightly increases for Cr (III) and somehow decreased with the gradual increase in initial concentration of Ni (II), as shown in Figure 3. The removal efficiency of Cr (III) is between 72.32 and 99.3% initial concentrations at 10 and 40 mg/L respectively. The percentage removal of Ni (II) was 80.73% at 10 mg/L and further increase in initial concentration led to a gradual decrease in the removal efficiency of
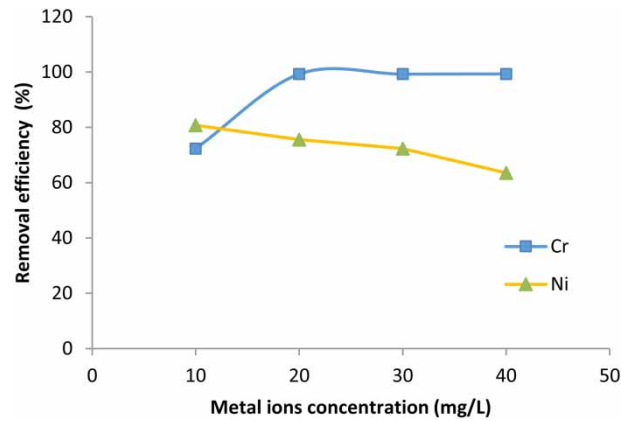
Figure 3 | Effect of metal ions concentration on removal efficiency.

Ni (II). The initial increase in Ni (II) removal may be due to the large number of vacant sites available on the adsorbent. As the concentration of metal ions increased, the number of vacant sites reduced until the surface of the adsorbent became saturated at equilibrium. Further increase in concentration after equilibrium meant a decrease in the ratio of the number of adsorbed ions to the initial number of ions, $(C_o – C_e)/C_o$, hence reduction in the percentage of ions removed.
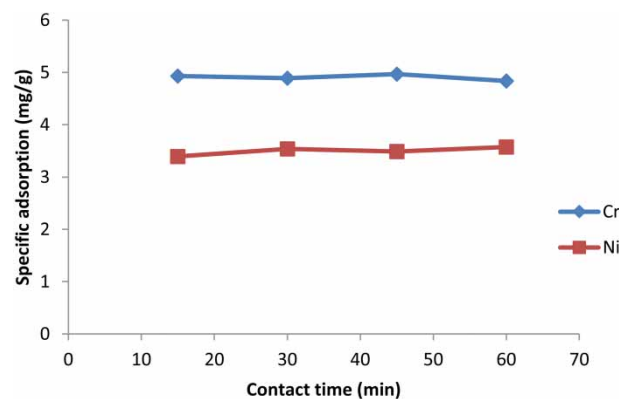
Effect of contact time

The time-dependent behavior of chromium and nickel adsorption was measured by varying the contact time between the adsorbate and adsorbent in the range of 15–60 min. The initial concentration of metal ions was 50 mg/L and the amount of adsorbent added was 0.5 g. The specific adsorption is determined using Equation (2).

$$q_e = \frac{(C_i − C_e)V}{m} \tag{2}$$

where, C_i is the initial metal ions concentration, C_e is the equilibrium concentration, V is the volume of solution and m is the mass of the adsorbent.

Figure 4 shows the effect of contact time on the adsorption of Cr (III) and Ni (II) metal ions. There is slightly increased specific adsorption with the increase in contact time from 15 to 45 min for both metal ions followed by a constant uptake on further increase in contact time. This indicates that equilibrium is attained at 45 min, showing that the adsorption sites are well exposed and the 60 min stirring time is enough for each batch to attain equilibrium (Heba & Sara 2014). However, the

Figure 4 | Effect of contact time on the adsorption of Cr (III) and Ni (II) ions onto clay sample.

adsorption of Cr (III) is higher than Ni (II) and the difference in adsorption capacity of the metal ions may be due to a number of factors, including hydration radii, hydration enthalpies, and solubility of cations (Jock *et al.* 2018).
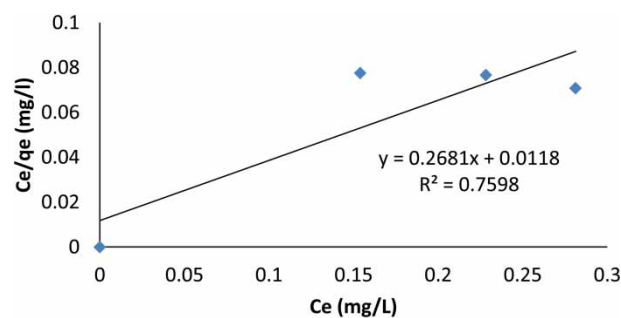
Adsorption isotherms

The isotherm models employed on the experimental data were Langmuir and Freundlich. The absorption parameters evaluated are given in Table 2. The Langmuir isotherm provides information on uptake capabilities and is capable of showing the equilibrium adsorption behaviour. The sorption isotherm is based on a homogeneous surface with identical active sites and restricted to a monolayer (Akpomie & Dawodu 2015). The Langmuir isotherm model is represented in Equation (3)

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{3}$$

Table 2 | Equilibrium isotherm constants for the adsorption process of Ni (II) and Cr (III)

Metal ions	Langmuir isotherm			Freundlich isotherm		
	q_{max}(mg/g)	b(l/mg)	R^2 (%)	n (l/mg)	K_F(mg/g).(L/mg)$^{1/n}$	R^2 (%)
Cr(III)	90.91	0.268	0.759	0.930	15.03	0.996
Ni(II)	7.937	0.517	0.994	1.712	0.5767	0.976

The parameter q_e (mg/g) is the quantity of metal ions adsorbed on the clay; q_m (mg/g) and b (L/mg) are the single-layer adsorption capacity and the Langmuir equilibrium constant respectively. The constants q_m and b were evaluated from the slope and intercept of the linear plot of C_e/q_e versus C_e in Figures 5 and 6. The Langmuir parameters are displayed in Table 2.

Figure 5 | Langmuir isotherm for Cr (III) adsorption on clay.
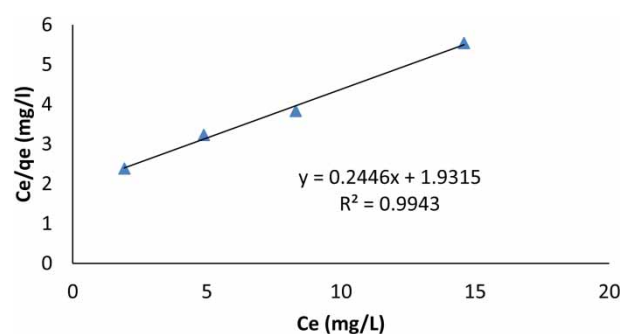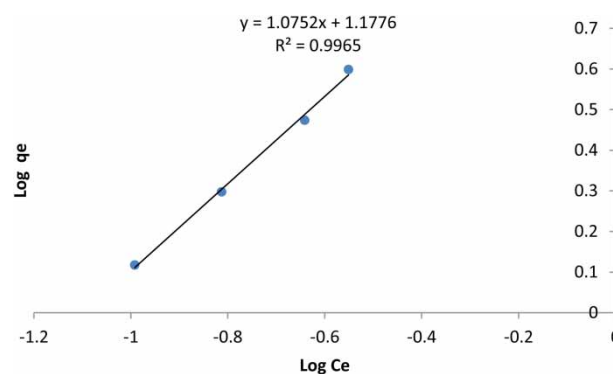

Figure 6 | Langmuir Isotherm for Ni (II) adsorption on clay.

The Freundlich isotherm is an empirical expression based on multilayer adsorption on a hetero-geneous surface and the linear form of this model is represented by Equation (4)

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

where, q_e is the equilibrium concentration of adsorbate in solid phase (mg/g) and C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L). K_F is the Freundlich constant related to the sorption capacity (mg/g) $(mg/L)^{1/n}$ and n is a dimensionless constant related to the adsorption intensity of the adsorbent.

Figures 7 and 8 shows the linear plot of log q_e versus log C_e with slope 1/n and intercepts log K_F. The Freundlich model parameters K_F and n are summarized in Table 2. The K_F value of 15.03 (mg/g)/ $(mg/L)^{1/n}$ for Cr (III) compared with 0.577 of Ni(II) indicates higher adsorption capacity of Cr (III) and this is in agreement with the higher uptake, q_m (99.91 mg/g), obtained using the Langmuir model. The significance of the n value is as follows: $n < 1$ (chemical process); $n = 1$ (linear) and $n > 1$ (physical process). Therefore, the value of n (0.93 L/mg) for Cr (III) represents chemical adsorption while the n-value (1.712) for Ni (II) shows physical adsorption (Marrakchi *et al.* 2010). The experimental data fitted well into the Freundlich model for Cr (III) having a regression coefficient (R^2) 0.996 and Langmuir isotherm for Ni (II) with $R^2 = 0.994$. It demonstrated that adsorption for all metal ions fitted the Langmuir isotherm as well as the Freundlich model. This might suggest that the surface of calcined bentonite is heterogeneous for chromium adsorption and homogenous for nickel ion. The uptake of chromium ion (90.91 mg/g) is higher than nickel ion (7.94 mg/g) and the order of adsorption is Cr (III) > Ni (II).

Figure 7 | Freundlich Isotherm for Cr (III) adsorption on clay.
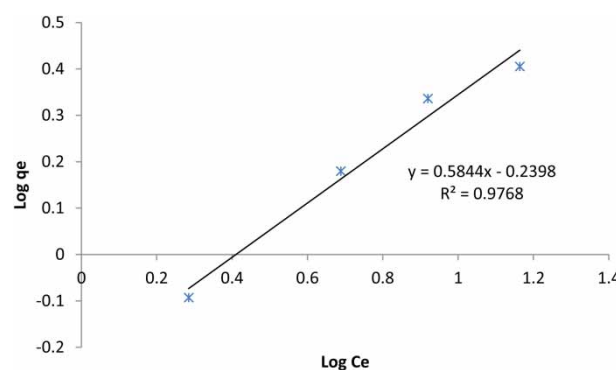
**Figure 8** | Freundlich Isotherm for Ni (III) adsorption on clay.

Adsorption kinetic

Adsorption kinetics deals with the rate of reaction and is an important characteristic that defines the efficiency of an adsorbent. Pseudo first order and pseudo second order kinetic models were applied to evaluate the adsorption mechanism of the experimental data. The linearize form of pseudo first order model is represented by Equation (5) and pseudo second order expressed in Equation (6)

$$\log (q_e - q_t) = \log q_e - \frac{1}{2.303} K_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where, K_1 (min^{-1}) is the first order rate constant and K_2 (g/mg min) is the second order rate constant of adsorption (min^{-1}), q_e and q_t are the amounts of metal ions adsorbed (mg/g) at equilibrium and time t respectively. The plots of $\log (q_e - q_t)$ against (t) for Cr (III) and Ni (II), though not represented here, gave poor fitted curves especially for Ni (II), indicating the adsorption process was not described by pseudo first order kinetic model. Figure 9 shows the linear plots of t/q_t vs. t for pseudo second order model and values of regression coefficients for both metal ions were very high ($R^2 = 0.999$). The parameters determined from the slope and intercept of the kinetic models for the adsorption of Ni (II) and Cr (III) are summarized in Table 3. Similarly, the higher values obtained for the uptake (q_e) further suggest that the pseudo-second order model is more likely to predict the kinetic behavior of the adsorption process. The applicability of the pseudo-second order kinetic model shows that the metal ion adsorption process is controlled by the chemisorption mechanism, indicating that the rate limiting step is based on chemical reaction between the metal ions and active sites of the bentonite adsorbent (Jock et al. 2016).
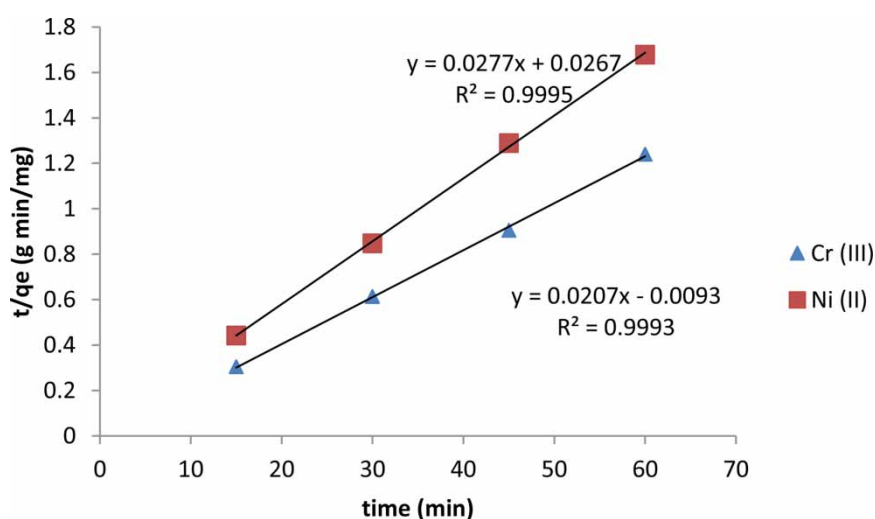
Figure 9 | Pseudo-second order model for the adsorption of Cr (III) and Ni (II) on bentonite clay.

Table 3 | Pseudo-first order and pseudo-second order kinetics for Ni (II) and Cr (III) adsorption onto bentonite clay

	Pseudo-first order			Pseudo-second order		
Metal ions	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/min mg)	R^2
Cr (III)	0.296	−0.0253	0.922	37.037	0.028	0.999
Ni (II)	1.104	0.0046	0.033	50.00	−0.044	0.999

Comparison of Cr (III) and Ni (II) metal ions adsorption capacity by different adsorbents

The adsorption capacity of a bentonite clay is influenced by its textural properties as well as the chemical nature of the adsorbent surface. Therefore, the possible mechanism of the adsorption of Cr (III) and Ni (II) metal ions on the calcined bentonite surface include surface functional groups, cation exchange, mesoporous texture and surface charge. Bentonites are polycations due to the presence of Ca^{2+}, Mg^{2+}, Na^+ and K^+ cations. These cations are exchangeable with Cr (III) and Ni (II) in the bulk solution or their amount is decreased in the adsorption process. The cations are exchanged with heavy metals.

Comparing the adsorption capacity of the calcined bentonite used with that of other adsorbents presented in Table 4, it is found that the present work gave a very favourable result especially in the uptake of Cr (III) metal ions. Higher adsorption capacity of Cr (III) onto chitosan and lower uptake by natural clay adsorbent was observed in comparison to the present study.

Table 4 | Comparison of adsorption capacity of Cr (III) and Ni (II) ions by various adsorbents

Metal adsorbed	Adsorbents type	q_{max} (mg/g)	References
Cr (III)	Chitosan	138.04	Pietrelli *et al.* (2020)
	Padina gymnospora	31.52	Mohamed *et al.* (2019)
	Sorghum bicolor	25.64	Adewoye *et al.* (2017)
	Retorted shale	25.23	Pimentel *et al.* (2011)
	Sepiolite	14.1	Padilla-Ortega *et al.* (2011)
	Lignin	17.97	Wu *et al.* (2008)
	Calcined bentonite	90.91	**Present work**
Ni (II)	Natural clay	6.25	Es-sahbany *et al.* (2019)
	Sorghum bicolor	47.62	Adewoye *et al.* (2017)
	Snail shell	78.34	Kamari *et al.* (2019)
	Peat	61.27	Bartczak *et al.* (2015)
	Activated carbon	69.49	Shrestha *et al.* (2014)
	LNC/MMT nanocomposite	94.86	Zhang & Wang (2015)
	Calcined bentonite	7.937	**Present work**

CONCLUSIONS

The removal of Cr (III) and Ni (II) from wastewater using a low-cost bentonite clay adsorbent was investigated. The clay was characterized and examined for its potential to adsorb metal ions from contaminated water in a batch mode. The study revealed that the adsorption process is influenced by initial concentration, contact time and temperature. The increase in these parameters increased the amount of metal uptake of Cr (III) and Ni (II) metal ions.

The Freundlich isotherm model obeyed the adsorption process of chromium metal ions, suggesting a heterogeneous nature of the bentonite adsorbent. The kinetic modelling performed showed that the pseudo-second order kinetics best fit the experimental data. The order of adsorption of heavy metals from single-metal solution is Cr (III) > Ni (II). The results show that the calcined bentonite clay is a promising adsorbent for the removal of nickel and chromium ions from wastewater.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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