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

Jock Asanja Alexandera,*, Oboh Oseribo Innocenta, Uwem Ekwere Inyanga, Ganchok Lawrenceb and Adeku Ojo©

a Department of Chemical and Petroleum Engineering, University of Uyo, Uyo, Nigeria

b Central Laboratory, Federal University Wukari, Nigeria

c Chemical and Petroleum Technique, Department of Science Laboratory Technology, University of Jos, Nigeria

*Corresponding author. E-mail: alsanja@gmail.com

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 (NiSO₄.6H₂O) and chromium tri oxide (Cr₂O₃) solutions were used as metal model compounds to evaluate the adsorption efficiency of the clay in a batch mode. The initial metal ions concentration range 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 adsorption equilibrium isotherm. The experimental data fitted well into Freundlich model for Cr (III) with regression coefficient (R²) of 0.996 and the Langmuir model for Ni (II) having R² 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. Theremoval of nickel and chromium using this clay has been found effective. The dataobtained 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, etc 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, etc are introduced in the environment through natural sources such as weathering and erosion of rocks; and anthropogenic sources such as chemical manufacturing plants, electroplating, battery, pesticides and fertilizers industries. Even at very low concentration of these metal ions tend to accumulate in living organisms, causing different health disorders in human and animals depending on the exposure rate and
dosage (Pandey & Tiwari 2015; Pandey & Ramontja 2016b; Adewoye et al. 2017). According to WHO (2011), 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 of 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, robust, 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 phyllosilicates and 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 microporores. 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, etc is required for improving its applicability for adsorption process (Prathiksha & Balakrishna 2018). Modified bentonite based composite offer a good alternative for use as adsorbents in wastewater remediation applications. Inorganic/organic nanocomposites posses properties of both organic and inorganic 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, activated carbon due to its high cost, 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, etc.

Bentonite clay exists in many parts of the world and these deposits have different properties due to their different geological location. The application of Dijah-Monkin bentonite as a local content in adsorption process has not been reported by researchers. Hence, this is one of the major reasons of 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 ions removal from 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 poses to humans and living creatures. The experiment was performed at different metal ion initial concentrations, contact time 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 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 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 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 thickened 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 a Q500 equipment TA Instruments, USA. Some physicochemical characteristics of the bentonite clay were 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 of nickel sulphate hexahydrate (NiSO₄·6H₂O) and chromium tri oxide (Cr₂O₃). Stock solutions of 1,000 mg/L concentrations for Cr (III) and Ni (II) metal ions were prepared by dissolving CrO₃ and NiSO₄·6H₂O 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 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 filter and the metal concentration of the 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 traced amount. The most abundant component of Si and Al in the sample confirmed the basic elements of 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 polyctionic 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 texture 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 and creating path for the pore volume is expected to enhance adsorption process (Zhu et al. 2016).

Table 1 | Pysicochemical properties of calcined bentonite

| Component (%) | Parameters |
|---------------|------------|
| Al Si K Ca Fe Ti Ag Mn | LOI (%) | P$^+$ | 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 aggregated mass of irregularly shape 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 aggregates, or open honeycomb texture (Zuzana et al. 2012).

Figure 2 shows the thermograph of the clay sample. The first weight loss 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 decomposition of
the clay structure. The low weight loss in the temperature range of dehydration step implied the changed 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).

\[
\% Ads = \frac{C_i - C_f}{C_i}
\]

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 concentration for Cr (III) and Ni (II) were varied from 10, 20, 30 to 40 mg/L using adsorbent amount of 0.5 g and contact time 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 increased in initial concentration led to gradual decrease in the removal efficiency of Ni (II). The
initial increased in Ni (II) removal may be due to large number of vacant sites available on the adsorbent. As the concentration of metal ion increased, the number of vacant site reduced until the surface of the adsorbent becomes saturated at equilibrium. Further increase in concentration after equilibrium meant a decrease in the ratio of number of adsorbed ions to the initial number of ions, \((C_0 - C_e)/C_0\), hence reduction in the percentage of ion 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).

\[
q_e = \frac{(C_i - C_e)V}{m}
\]  

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

**Figure 4** shows the effect of contact time on the adsorption Cr (III) and Ni (II) metal ions. There is slightly increased in specific adsorption with the increased in contact time from 15 to 45 min for both metal ions followed by a constant uptake on further increased 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 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 to the experimental data were Langmuir and Freundlich. The absorption parameters evaluated are given in Table 2. Langmuir isotherm provides information on uptake capabilities and is capable of showing the equilibrium adsorption behaviour. The sorption isotherm is based on the homogeneous surface by identical active sites and restricted to a monolayer (Akporie & Dawodu 2015). The Langmuir isotherm model is represented in Equation (3)

\[ \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \]  

(3)

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

| Metal ions | Langmuir isotherm | Freundlich isotherm |
|------------|-------------------|---------------------|
|            | \( q_m^{\text{max}} (\text{mg/g}) \) | \( b (\text{L/mg}) \) | \( R^2 (\%) \) | \( n (\text{L/mg}) \) | \( K_F (\text{mg/g})(\text{L/mg})^{1/n} \) | \( R^2 (\%) \) |
| 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 heterogeneous surface and the linear form of this model is represented by Equation (4)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (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 show 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 Langmuir model. The significance of \( n \) value 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 \( n \)-value (1.712) for Ni (II) shows physical adsorption (Marrakchi et al. 2010). The experimental data fitted well into Freundlich model for Cr (III) having 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 fit 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 define 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)

\[
\log \left( \frac{q_e - q_t}{q_e} \right) = \log q_e - \frac{1}{2.303} K_1 t
\]

(5)

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e}
\]

(6)

where; \( K_1 \) (min \(^{-1}\)) is the first order rate constant and \( K_2 \) (g/mg min) is 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 describe 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 suggests that the pseudo second order model is more likely to predict kinetic behavior of adsorption process. The applicability of 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 site of 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

| Metal ions | Pseudo first order | Pseudo second order |
|------------|--------------------|---------------------|
|            | \( q_e \) (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     | 37.057           | 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 adsorbent surface. Therefore, the possible mechanism of the adsorption of Cr (III) and Ni (II) metal ions on calcined bentonite surface include surface functional groups, cation exchange, mesoporous texture and surface charge. Bentonite 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 decreased in 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            | \(q_{\text{max}} \) (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. They 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.
REFERENCES

Adewoye, L. T., Mustapha, S. I., Adeniyi, A. G., Tijani, J. O., Amoloye, M. A. & Ayinde, L. J. 2017 Optimization of nickel (ii) and chromium (iii) removal from contaminated water using sorghum bicolor. Nigerian Journal of Technology 36(3), 960. http://dx.doi.org/10.4314/njt.v36i3.41.

Ahmed, A. S., Salahudeen, N., Ajnonoh, C. S., Hamza, H. & Ohikere, A. 2012 Studies on the mineral and chemical characterization of Pindiga bentonite clay. Petroleum Technology Development Journal 1, 2–8.

Alkpmie, G. K. & Dawodu, A. F. 2015 Potential of a low-cost bentonite for heavy metal abstraction from binary component system. Beni-Suef University Journal of Basic and Applied Sciences 1–13. http://dx.doi.org/10.1016/j.bjbas.2015.02.002.

Araujo, A. L. P., Bertagnolli, C., Silver, M. G. C., Gimenes, M. L. & Barros, M. A. S. 2013 Zinc adsorption in bentonite clay: influence of pH and initial concentration. Acta Scientiarum Technology 35(2), 325–332.

Bartczak, P., Norman, M., Klapiszewski, L., Karwanska, N., Kawalec, M., Baczyska, M., Wysokowski, M., Zdarta, J., Ciesieleczk, F. & Jesionowski, T. 2015 Removal of nickel(II) and lead(II) ions from aqueous solution using peat as a low-cost adsorbent: a kinetic and equilibrium study. Arabian Journal of Chemistry 11, 1210–1222. doi.org/10.1016/j.arabjc.2015.07.018.

Bertagnolli, C., Kleinmubing, S. J. & Silva, M. G. C. 2011 Preparation and characterization of a Brazilian bentonite clay for removal of copper in porous beds. Applied Clay Science 53(1), 73–79. doi:10.1016/j.clay.2011.05.002.

Dogara, K., James, Y. & Manaseh, Y. B. 2017 Assessment of heavy metals concentration in drinking water samples from selected areas of Kaura local government area of Kaduna State, Nigeria. Bayero Journal of Pure and Applied Sciences 10(1), 509–515.

Es-sahbany, H., Berradi, M., Nikhill, S., Hisisou, R., Allauoi, M., Loutfi, M., Bassir, D., Belfaquir, M. & El Youbi, M. S. 2019 Removal of heavy metals (nickel) contained in wastewater-models by the adsorption technique on natural clay. Materials Today: Proceedings 13, 866–875.

Hassan, S. B. 2005 Modern Refractories-Production, Properties, Testing and Applications, 1st edn. Timo Commercial Printers, Zaria, pp. 1–57.

Heba, H. E. & Sara, M. 2014 Removal of heavy metals via adsorption using natural clay material. Journal of Environment and Earth Science 4(19), 2224–3216.

Jock, A. A., Muhammad, A. A. Z., Abdulsalam, S., El-Nafaty, U. A. & Aroke, U. O. 2016 Insight into kinetics and thermodynamics properties of multicomponent lead(II), cadmium(II) and manganese(II) adsorption onto Dijah-Monkin bentonite clay. Particulate Science and Technology 1–12. http://dx.doi.org/10.1080/02726351.2016.1276499.

Jock, A. A., Muhammad, A. A. Z., Abdulsalam, S., El-Nafaty, U. A. & Aroke, U. O. 2018 Isothermal study of lead(II), manganese(II) and cadmium(II) adsorption by Nigerian bentonite clay single and multimetal solutions. Particulate Science and Technology 1–12. https://doi.org/10.1080/02726351.2017.1404514.

Kamari, A., Shamsudin, R., Eljiedi, A. A. A., Yusoff, S. N. M., Wong, S. T. S., Ishak, S., Jumadi, J., Abdulsalam, M. M. & Kumaran, S. 2019 Treatment of electronics industry effluent using low-cost and commercial adsorbents: a comparative study. Journal of Physics: Conference Series 1397, 1–10. doi:10.1088/1742-6596/1397/1/012022.

Kukwa, D., Bayereve, R. & Ikene, C. (2014). Characterization of primitive clays from Katsina Ala and Mukurdi, Benue State-Nigeria. Chemistry and Materials Research 6 (4), 115–121.

Mansri, A., Benabadj, I. K., Desbrieres, J. & Francois, J. 2009 Chromium removal using modified poly(4-vinylpyridinium) bentonite salts. Desalination 245, 95–107. https://doi.org/10.1016/j.desal.2008.06.012.

Marrakchi, F., Hameed, B. H. & Hummade, H. E. 2010 Mesoporous biohybrid epichlorohydrin crosslinked chitosan/carbon-clay adsorbent for effective cationic and anionic dyes adsorption. International Journal of Biological Macromolecules 43, 1079–1086. https://doi.org/10.1016/j.ijbiomac.2020.07.032.

Mohamed, S. M., Soliman, N. K., Abdelheem, A. D., Ramadan, A. A., Elghandour, H. A. & Ahmed, A. S. 2019 Adsorption of Cd²⁺ and Cr³⁺ ions from aqueous solutions by using residue of Padina gymnospora waste as promising low-cost adsorbent. Heliyon 5, 1–32. doi:10.1016/j.heliyon.2019.e01287.

Naser, M. A., Waffa, M., Omar, A., Jameel, A. A. H. & Manawwer, A. 2019 Adsorptive application o montmorillonite clay for the removal of ag(I) and Cu(II) from Aqueous Medium. Hindawi Journal of Chemistry 1–7. https://doi.org/10.1155/2019/7129014.

Nwafulugo, F. U., Adefila, S. S., Olawale, A. S. & Ajayi, O. A. 2014 Environmental impact and removability of selected heavy metals from petroleum wastewater using zeolite 4A-metakaolin matrices. Journal of Environmental Science and Water Resources 3(6), 132–143.

Padilla-Ortega, E., Leyva-Ramos, R., Mendoza-Barron, J., Guerrero-Coronado, M. R., Jacobo-Azuara, A. & Aragon-Pina, A. 2011 Adsorption of heavy metal ions from aqueous solution onto sepiolite. Adsorption Science & Technology 29(6), 569–584.

Pandey, S. 2017 A comprehensive review on recent developments in bentonite-based materials used as adsorbents for wastewater treatment. Journal of Molecular Liquids 241, 1091–1113.

Pandey, S. & Mishra, B. S. 2011 Sol–gel derived organic–inorganic hybrid materials: synthesis, characterization and applications. Journal of Sol-Gel Science and Technology 59, 73–94. DOI 10.1007/s10971-011-2465-0.

Pandey, S. & Tiwari, S. 2015 Facile approach to synthesize chitosan based composite characterization and cadmium (II) ion adsorption studies. Carbohydrate Polymers 134, 646–656.

Pandey, S. & Ramontja, J. 2016a Recent modifications of bentonite clay for adsorption applications. Focus on Sciences 2(4), 1–10.
Pandey, S. & Ramontja, J. 2016b Turning to nanotechnology for water pollution control: applications of nanocomposites. Focus Sciences 2(3), 1–10.
Pandey, S. & Ramontja, J. 2016c Natural bentonite clay and its composites for dye removal: current state and future potential. American Journal of Chemistry and Applications 3(2), 8–19.
Pandey, S., Do, Y. J., Kim, J. & Kang, M. 2020a Fast and highly efficient removal of dye from aqueous solution using natural locust bean gum based hydrogels as adsorbent. International Journal of Biological Macromolecules 143, 60–75.
Pandey, S., Fosso-Kankeu, E., Spiro, J. M., Waander, F., Kumar, N., Ray, S. S., Kim, J. & Kang, M. 2020b Equilibrium, kinetic, and thermodynamic studies of lead ion adsorption from mine wastewater onto MoS2-clinoptilolite composites. Materials Today Chemistry 18, 1–11.
Pietrelli, L., Francolini, I., Piozzi, A., Sighicelli, M., Silvestro, I. & Vocciante, M. 2020 Chromium (III) removal from wastewater by Chitosan flakes. Applied Sciences 10, 1925. doi:10.3390/app10061925.
Pimentel, P. M., Oliveira, R. M. P. B., Melo, D. M. A., Melo, M. A. F., Assuncao, A. L. C. & Gonzales, G. 2011 Adsorption of chromium ions on oil shale waste. Brazilian Journal of Petroleum and Gas 5(2), 65–73. doi:10.5419/bjpg2011-0008.
Prathiksha, P. P. & Balakrishna, P. 2018 A review on removal of heavy metal ions from waste water using natural/modified bentonite. MATEC Web of Conferences 144, 1–13. https://doi.org/10.1051/matecconf/201814402021.
Saika, B. & Parthasarathy, G. 2010 Fourier transform infrared spectroscopic characterization of kaolinite from Assam and Meghalaya, Northeastern India. Journal of Modern Physics 1(4), 206–210. doi:10.4236/jmp.2010.14031.
Shrestha, M. R., Varga, M., Varga, I., Yadav, P. A., Pokharel, P. B. & Pradhananga, R. R. 2014 Removal of Ni (II) from aqueous solution by adsorption onto activated carbon prepared from Lapsi (Choerospondias axillaris) seed stone. Journal of the Institute of Engineering 9(1), 166–174. doi: 10.3126/jie.v9i1.10680.
Ugwu, M. I. & Igboke, A. O. 2019 Sorption of Heavy Metals on Clay Minerals and Oxides: A Review, Advanced Sorption Process Applications. Intechopen, 1–24. DOI: http://dx.doi.org/10.5772/intechopen.80989.
Wu, Y., Zhang, S., Guo, X. & Huang, H. 2008 Adsorption of chromium(III) on lignin. Bioresource Technology 99, 7709–7715. doi: 10.1016/j.biortech.2008.01.069.
Zhang, X. & Wang, X. 2015 Adsorption and desorption of Nickle (II) ions from aqueous solution by a lignocellulose/montmorillonite nanocomposite. PLoS ONE 10(2), 1–21. doi:10.1371/journal.pone.0117077.
Zhu, R., Chen, Q., Zhou, Q., Xi, Y., Zhu, J. & He, H. 2016 Adsorbents based on montmorillonite for contaminant removal from water: a review. Applied Clay Science 123, 239–258. doi:10.1016/j.clay.2015.12.024.
Zuzana, O., Annamaria, M., Silva, D. & Jaroslav, B. 2012 Effect of thermal treatment on bentonite properties. Arhiv Za Tehnicke Nauke 7(1), 49–56.

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