ORIGINAL ARTICLE

Treatment of an automobile effluent from heavy metals contamination by an eco-friendly montmorillonite

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ABSTRACT

Unmodified montmorillonite clay was utilized as a low cost adsorbent for the removal of heavy metals from a contaminated automobile effluent. Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy were used to characterize the adsorbent. Batch sorption experiments were performed at an optimum effluent pH of 6.5, adsorbent dose of 0.1 g, particle size of 100 μm and equilibrium contact time of 180 min. Thermodynamic analysis was also conducted. Equilibrium data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models. A heterogeneous surface of the adsorbent was indicated by the Freundlich model. The Langmuir maximum adsorption capacity of the montmorillonite for metals was found in the following order: Zn (5.7 mg/g) > Cu (1.58 mg/g) > Mn (0.59 mg/g) > Cd (0.33 mg/g) > Pb (0.10 mg/g) ≈ Ni (0.10 mg/g). This was directly related to the concentration of the metal ions in solution. The pseudo-first order, pseudo-second order, intraparticle diffusion and liquid film diffusion models were applied for kinetic analysis. The mechanism of sorption was found to be dominated by the film diffusion mechanism. The results of this study revealed the potential of the montmorillonite for treatment of heavy metal contaminated effluents.

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Introduction

The pollution of the environment with toxic substances has been on the increase in recent years as a result of the rapid growth of industries. Most industries such as automobile, mining, electroplating, iron–steel and battery industries utilize substances containing heavy metals [1]. Subsequently, these heavy metals are discharged into the environment from the effluents obtained from the industries. Although small amounts of some heavy metals are necessary for the normal development of
biological cycles, most of them are toxic at high concentrations [2]. The release of heavy metals into the environment poses a serious threat to aquatic lives, plants and humans due to their persistence, non-biodegradability and bio-accumulation in the food chain. Therefore, the removal of these metals from industrial effluents is necessary to maintain environmental quality [3]. Several techniques have been utilized for heavy metal removal, which include solvent extraction, filtration, ion-exchange, coagulation, sedimentation, oxidation and activated carbon adsorption [4]. However, these techniques have the disadvantages of high cost, low removal efficiency and the problem of secondary contamination. As a result, many researchers have utilized low cost, eco-friendly and highly efficient adsorbents for removal of heavy metals from effluents. These adsorbents include biomass materials, clays, charcoal, sludge ash, microorganisms and lateritic materials, just to mention a few [5].

Montmorillonite has been found to be suitable for heavy metals adsorption through cation exchange mechanism in the interlayer and the formation of inner sphere complexes through Si–O and Al–O groups at the clay particle edges [6–8]. However, most studies in literature have not been focused on the use of montmorillonite for adsorption of heavy metals from automobile effluent in particular. This study is therefore focused on the removal of heavy metals from a contaminated automobile effluent unto a montmorillonite. The automobile industry (Innowon) is located in Nnewi, Anambra State, Nigeria and was chosen due to the reasonably high metal concentration. Similarly, the montmorillonite was utilized because it is found in an abundant amount in Nigeria and can be utilized as a low cost and eco-friendly adsorbent.

The montmorillonite was used without any modification (chemical or physical) in order to keep the process cost low. The effect of various experimental conditions such as pH, adsorbent dose, contact time and particle size was investigated. Equilibrium, kinetic and thermodynamic analyses were also determined to understand the adsorption mechanism.

**Experimental**

**Processing of the montmorillonite**

The montmorillonite was collected from Oji river local government area of Enugu State, Nigeria. It was immersed in excess distilled water in a pretreated plastic container and stirred uniformly for proper mixing. Thereafter, the mixture was passed through a mesh sieve of size 500 μm to get rid of plant materials and other suspended particles. The obtained filtrate was kept for 24 h to settle after which excess water was decanted. The residue was sundried and then dried in an oven at 378 K for 4 h. The dried clay was then pulverized and passed through different mesh sieves of sizes 100–500 μm to obtain the unmodified montmorillonite clay (UMC).

**Physicochemical analysis**

The automobile effluent was collected from the discharge outlet of Innoson automobile industry located in Nnewi, Anambra State, Nigeria. The effluent was stored at 277 K in a refrigerator. Sample collection was based on the technique described [9]. The physicochemical analysis of the effluent was determined using standard methods [10]. Heavy metal concentration in the effluent was analyzed by the use of the Atomic absorption spectrophotometer (AAS) (Buck scientific model 210VGP). All the reagents used were of analytical grade, obtained from Sigma Aldrich (Steinheim, Germany) and used without further purification. Chemical composition of UMC was determined by the AAS after digestion of the sample with nitric acid. The cation exchange capacity (CEC) of the adsorbent was obtained by the ammonium acetate method [11], while the pH point of zero charge was determined by the method described [12]. The slurry pH was obtained as described previously [5]. X-ray diffractometer (RADC100 MD 10 model) was utilized for the X-ray diffraction (XRD) analysis. The Fourier transform infrared (FTIR) of UMC was taken by the help of the Fourier transform infrared spectrophotometer (Shimadzu FTIR 8400s). BET surface area and pore properties of UMC were obtained by nitrogen adsorption–desorption isotherms by the use of the micromeritics ASAP 2010 model analyzer. Scanning electron microscopy (SEM) (Hitachi S4800 model) was used to determine the morphology of the adsorbent.

**Effluent treatment**

The automobile effluent was treated by the batch adsorption technique by contacting 0.1 g of the adsorbent with 50 ml of effluent solution in 100 ml plastic bottles under optimum conditions as described: The effect of pH was studied by adjusting the pH of the effluent from 2 to 8 by the drop wise addition of 0.1 M NaOH or 0.1 M HCl when required before the addition of the adsorbent, this was performed using an adsorbent particle size of 100 μm, contact time 180 min and temperature of 300 K. The influence of adsorbent dose was performed using different doses of 0.1–0.5 g, effluent pH 6.5, adsorbent particle size 100 μm and contact time of 180 min at temperatures of 300, 313 and 323 K. Temperature regulation was performed by the use of a thermostat water bath. By varying the particle size of the adsorbent from 100 to 500 μm the influence of adsorbent particle size on adsorption was investigated, this was performed at pH 6.5, adsorbent dose 0.1 g, contact time 180 min and temperature of 300 K. Finally, the effect of contact time on adsorption was performed at an effluent pH of 6.5, particle size 100 μm at temperatures of 300, 313 and 323 K by varying the contact time of experiment from 10 to 300 min.

At the end of the given contact time for each experiment, the solution was filtered and the concentration of heavy metals remaining in the effluent, , was determined by the mass balance equation given as:

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

where \( q_e \) (mg/g) is the amount of heavy metal adsorbed per unit weight of UMC, \( C_i \) (mg/L) is the initial concentration of heavy metals in the effluent, \( C_e \) (mg/L) is the equilibrium concentration of heavy metals remaining in the effluent, \( v \) (L) is the volume of effluent solution used and \( m \) (g) is the mass of UMC utilized for adsorption.

**Isotherm modeling**

The equilibrium isotherm model analysis was studied by the application of the Langmuir, Freundlich, Temkin and
Dubinin–Radushkevich models. The Langmuir isotherm describes a monolayer adsorption onto a homogenous adsorbent surface. The linear form of the Langmuir equation is given as follows [13]:

\[ \frac{C_e}{q_e} = 1/q_L K_L + \frac{C_e}{q_L} \]  

(2)

where \( q_L \) (mg/g) is the Langmuir maximum monolayer adsorption capacity, \( K_L \) (L/mg) is the Langmuir adsorption constant. A dimensionless constant or separation factor (\( R_L \)) of the Langmuir isotherm was utilized to describe the adsorption and was calculated from the equation:

\[ R_L = \frac{1}{1 + K_L C} \]  

(3)

The value of \( R_L \) indicates the type of adsorption to be irreversible (\( R_L = 0 \)), favorable (\( 0 < R_L < 1 \)), linear (\( R_L = 1 \)) or unfavorable (\( R_L > 1 \)).

The Freundlich isotherm model is based on a multilayer adsorption onto a heterogeneous surface. The linear form of the Freundlich equation is given as follows [14]:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(4)

where \( K_F \) (L/g) is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent, while \( n \) is a dimensionless constant related to the adsorption intensity.

The Temkin isotherm model is based on the assumption that the free energy of adsorption is a function of the surface coverage and the linear form is presented as follows [15]:

\[ q_e = B' \ln N + B' \ln C_e \]  

(5)

where \( A \) (L/mg) is the equilibrium binding constant, the constant \( B = RT/b_y \) (mg/g) is related to the heat of adsorption, \( R \) is the ideal gas constant (8.314 J/mol K), \( T \) (K) is the absolute temperature and \( b_y \) is the Temkin isotherm constant.

The Dubinin–Radushkevich (D–R) isotherm was applied to identify the nature of adsorption as either physical or chemical process. The linear form of the isotherm is given as follows [16]:

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \]  

(6)

where \( q_m \) (mg/g) is the D–R maximum adsorption capacity, \( \beta \) (mol^2/J^2) is related to the mean free energy of adsorption and \( \varepsilon \) (kJ/mol) is the Polanyi potential \( [\varepsilon = RT \ln(1 + 1/C_e)] \). The constant \( \beta \) is related to the energy of adsorption \( E \) (kJ/mol) by the following equation:

\[ E = 1/(2\beta)^{1/2} \]  

(7)

When the value of \( E \) falls in the range of 8–16 kJ/mol the adsorption is said to be chemically controlled and it is dominated by physical mechanism if \( E < 8 \) kJ/mol [17].

Kinetic modeling

The kinetic mechanism of the adsorption process was investigated by application of the pseudo-first order, pseudo-second order, intraparticle diffusion and liquid film diffusion model rate equations.

The pseudo-first order kinetic model or Largergren equation is expressed as follows [18]:

\[ \log(q_e - q_t) = \log q_e - \left( K_i/2.303 \right)t \]  

(8)

where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amount adsorbed at equilibrium and time \( t \) (min), respectively. \( K_i \) (min^-1) is the pseudo-first order rate constant of adsorption.

The pseudo-second order kinetic model is given as follows [19]:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  

(9)

where \( K_2 \) (g/mg/min) is the pseudo second order rate constant. The initial sorption rate \( h \) (mg/g min) was calculated from the equation:

\[ h = K_2 q_e^2 \]  

(10)

Metal ions are transported from the aqueous phase to the surface of an adsorbent and can diffuse into the interior if favorable. The intraparticle diffusion equation would then be applicable and is given as follows [20]:

\[ q_t = K_d t^{1/2} + C \]  

(11)

where \( K_d \) (mg/min^{1/2}) is the intraparticle diffusion rate constant and \( C \) represents the intercept. If the plot of \( q_t \) versus \( t^{1/2} \) is linear then the intraparticle diffusion is involved in the mechanism. Also, if the plot passes through the origin (\( C = 0 \)) then intraparticle diffusion is the sole rate controlling step of the adsorption process [17].

When the transport of the adsorbate from the liquid phase to the solid phase boundary plays the most significant role in adsorption, then the liquid film diffusion model can be applied [20]:

\[ \ln(1 - F) = -K_{df} t + Y \]  

(12)

where \( F = q_t/q_e \) is the fractional attainment of equilibrium, \( K_{df} \) (mg/g min) is the film diffusion adsorption rate constant and \( Y \) is the intercept. A linear plot of \( -\ln(1 - F) \) versus \( t \) suggest that the kinetics of adsorption involves a film diffusion mechanism. Furthermore, if the plot is linear with \( Y = 0 \) then film diffusion is the sole rate controlling mechanism.

Adsorption thermodynamics

The thermodynamic parameters such as the standard free energy (\( \Delta G^0 \)), Enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) were determined to evaluate the feasibility of adsorption by the application of the following equations [5]:

\[ \Delta G^0 = -RT \ln K_c \]  

(13)

\[ \ln K_c = -\left( \frac{\Delta H^0}{RT} \right) + \left( \frac{\Delta S^0}{R} \right) \]  

(14)

where \( K_c = C_a/C_e \) is the distribution coefficient, \( C_a \) (mg/L) and \( C_e \) (mg/L) represent the concentration of heavy metals adsorbed and that remaining in solution at equilibrium, respectively. \( T \) (K) is the absolute temperature and \( R \) is the gas constant. \( \Delta H^0 \) and \( \Delta S^0 \) were evaluated from the slope and intercept of the linear plot of \( \ln K_c \) versus \( 1/T \).

Results and discussion

Physicochemical characteristics

The physicochemical characterization of the automobile effluent is shown in Table 1. pH is a simple parameter but is extremely important, since most of the chemical reactions in aquatic environment are controlled by any change in its value. Aquatic organisms are sensitive to pH changes and biological treatment requires pH control or monitoring. Also the toxicity of heavy
The most important measure of water quality is the dissolved oxygen (DO) [24]. Hydrogen sulfide is formed under conditions of deficient oxygen in the presence of organic materials and sulfate. The effluent waste discharge to surface water source is largely determined by the oxygen balance of the system and its presence is essential in maintaining life within a system. Dissolved oxygen concentration in unpolluted water normally range between 8 to 10 mg/L and the concentration below 5 mg/L adversely affect aquatic life [25] because the organisms become stressed, suffocate and die. The DO values obtained for the effluent were below the recommended WHO standard (5 or more) [21]. Similarly, the Biochemical Oxygen Demand (BOD) and chemical oxygen demand (COD) are very useful parameters in assessing the quality of an effluent. The consequences of high BOD and COD are the same as low DO; both parameters affect directly the amount of DO. The greater the BOD and COD the more rapidly oxygen is depleted in the water; this means a corresponding decrease in the DO value and the less oxygen available to aquatic life. BOD is simply a measure of the amount of oxygen required by bacteria or microorganisms for breaking down to simpler substances of the decomposable organic matter present in any water, wastewater or treated effluent [26]. The greater the decomposable organic matter the greater the oxygen demand and the greater the BOD [27]. The COD is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. Both BOD and COD are used to measure the concentration of organic matter present in any water. The BOD and COD values of the effluent are much higher than the WHO recommended limit of 15 and 40 mg/L respectively, which may lead to a corresponding increase in their receiving water bodies and consequently have an adverse effect on aquatic lives [21]. The high values obtained could be attributed to an increase in the addition of both organic and inorganic contaminants entering the systems from the industrial processes.

Most importantly, the heavy metals concentration of Pb, Zn, Cu, Cd, Ni and Mn exceeded the maximum WHO permissible limits of 0.05, 5.0, 1.0, 0.005, 0.05 and 0.1 mg/L respectively [21]. This indicates a harmful effect to the environment and aquatic life, since the effluents are capable of having a corresponding increase in the concentration of these metals in their receiving water bodies. Chromium however recorded a lower concentration than the WHO limit of 0.05 mg/L [21]. Due to the high concentrations of heavy metals in the automobile effluent, it was therefore necessary to investigate the potential of UMC as an adsorbent for the removal of these metals from solution.

Data obtained from the physicochemical characterization of UMC are shown in Table 2. The montmorillonite recorded a BET surface area ($S_{\text{BET}}$) of 55.76 $m^2/g$, a total pore volume (TPV) of 0.0688 $cm^3/g$ and an average pore diameter (APD) of 49.35 Å [8]. As discussed previously [8], the $S_{\text{BET}}$ is higher than that reported by Guo et al. [7] of 26.33 $m^2/g$ but close to that (61 ± 2 $m^2/g$) reported by Macht et al. [28]. Many factors contribute to the differences in $S_{\text{BET}}$ values of montmorillonites which include the purity and type of montmorillonite, the saturating cation, the out gassing temperature and the preparatory treatment received by the sample [8].

### Table 2 Physicochemical characterization of the montmorillonite.

| Parameter   | Value  |
|-------------|--------|
| $SiO_2$ (%) | 47.32  |
| $Al_2O_3$ (%) | 25.91  |
| $Fe_2O_3$ (%) | 2.14   |
| $CaO$ (%) | 3.39   |
| $K_2O$ (%) | 1.07   |
| $Na_2O$ (%) | 2.86   |
| $MgO$ (%) | 3.14   |
| $TiO_2$ (%) | 0.12   |
| $MnO$ (%) | 0.43   |
| $LOI$ (%) | 13.56  |
| Si/Al ratio | 1.83   |
| $S_{\text{BET}}$ ($m^2/g$) | 55.76  |
| TPV ($cm^3/g$) | 0.0688 |
| APD (Å) | 49.35  |
| pH$_{pzc}$ | 3.7    |
| Slurry pH | 4.2    |
The nature of the functional groups on the surface of UMC before and after adsorption was determined by the FTIR spectra as shown in Fig. 1. Absorption bands at 3697.66 cm\(^{-1}\) and 3620.51 cm\(^{-1}\) are assigned to the inner surface –OH stretching of kaolinite, which suggest the presence of kaolinite in the sample [8]. The outer –OH stretching vibration was indicated by the bands at 3441.12 cm\(^{-1}\) and 3410.26 cm\(^{-1}\). Absorption at 1627.97 cm\(^{-1}\) represents the –COO– symmetric stretching vibration. The smectite structure was indicated by the occurrence of the outer –OH stretching and the symmetric –COO– stretching vibration [29]. Absorptions at 1114.89–1095.6 cm\(^{-1}\) correspond to the Si–O bending vibration while the stretching vibrations were observed at 796.63 cm\(^{-1}\) and 694.4 cm\(^{-1}\) [30]. The Al–O bending vibration was observed at 912.36 cm\(^{-1}\), and the Al–O–Si skeletal vibration at 536.23, 470.65 and 430.14 cm\(^{-1}\) [8]. After the adsorption of heavy metals from the automobile effluent, there were bands shifts in the surface groups which indicate the active participation of the surface functional groups in the adsorption process. This was inferred by the outer surface –OH band shift from 3441.12 to 3439.19 cm\(^{-1}\), the occurrence of bands at 2360.95 and 2000.25 cm\(^{-1}\) may have been acquired from adsorption of some organic containing substances in the effluent. The involvement of the symmetric –COO– groups was indicated by absorption shifts from 1627.97 and 1629.9 cm\(^{-1}\). Bands shift from 1097.53 to 1095.6 cm\(^{-1}\), 1031.95 to 1033.88 cm\(^{-1}\) and 1006.88 cm\(^{-1}\) to 1008.8 cm\(^{-1}\) were observed for the Si–O bending vibration. The Al–O–Si linkages were also involved as indicated by the shifts from 536.23 to 538.16 cm\(^{-1}\) and 430.14 to 426.28 cm\(^{-1}\).

The d-spacing values presented by the XRD spectra of UMC in Fig. 2 showed 2\(\theta\) values of 23.74 and 24.58, indicating montmorillonite as the major constituent and also the presence of quartz as minute mineral. Finally, the SEM image of UMC as shown in Fig. 3 revealed a porous structure which is a requirement for any potential adsorbent.

Influence of pH

The initial pH of a solution is a very important factor to be considered in adsorption studies as it affects the surface charge of an adsorbent. As a result, characterization of the effect of pH on adsorption was investigated in this study. The result of pH on the removal of heavy metals from the automobile effluent is shown in Fig. 4. An increase in the adsorption of metals with increase in effluent

![Fig. 1](image-url) The Fourier transform infrared spectra of the montmorillonite (A) before adsorption (B) after adsorption of metal ions.
pH was observed. Considering the affinity of UMC for metal ions, the following trend was obtained: Zn > Cu > Mn > Cd > Pb > Ni. It was noticed that this trend corresponds to the metals concentrations in the effluent with the highest concentration obtained for Zn and the lowest for Ni (Table 1). It has been reported that the differences in
adsorption trend of the metal ions may be attributed to differences in the behaviors among these metals or their ions in solution [31]. This is mainly due to differences in the properties such as ionic size, electro-negativity, strength of acidity of the metals and the pK_{OH} (negative log of hydrolysis constant) [31]. However, in this case the initial metal concentration in the effluent dominates the above mentioned factors in determining the amount of metal ions adsorbed. Such factors are usually significant, if the metal ions in solution are presented in the same concentration. We have reported in our previous study that the initial concentration of metal ions in solution plays a major role in determining the amount of metal ions adsorbed [5]. This is because higher concentration generates a greater driving force for more metals to undergo an interaction with the adsorbent. In fact it also implies the availability of more metal ions in solution to be adsorbed. Therefore if there are changes in the effluent, metals concentration would change, resulting in a change in the adsorption capacity of the adsorbent for each metal depending on its concentration. The low adsorption capacity of UMC for Pb(II) and Ni(II) is simply due to the very low concentration of these metals in the effluent. Also, significant adsorptions of metal ions were achieved at higher pH values greater than the pH_{pzc} of 3.7 at which the surface of the adsorbent acquired a negative charge. The low adsorption of metal ions at lower pH values is due to the high concentration of H^+ ions in solution which competes with the metals for the active sites of the adsorbent. However, as the pH of the solution increases, the number of H^+ ions decreases, thereby making more active sites available for metal sorption due to decreased competition with the protons. At an effluent pH of 5.0, Cd ion showed a decrease; also slight decrease in adsorption of Mn and Cu was obtained at 6.0. The natural pH of the effluent of 6.5 was used in this study for all subsequent experiments because optimum removal of all metal ions was achieved at this pH range and higher values were avoided to prevent metal precipitation as hydroxides.

**Influence of adsorbent dose**

The adsorbent weight is an important factor in determining the capacity of the adsorbent for a given adsorbate concentration and volume of solution. The influence of the weight of UMC on heavy metal removal from the effluent was studied at temperatures of 300, 313 and 323 K. The result is shown in Fig. 5. It can be seen that for all temperatures studied, a decrease in the equilibrium adsorption capacity per unit mass of UMC for all metal ions with increase in the weight of adsorbent was recorded. The decrease in adsorption capacity is attributed to the higher UMC dose providing more active adsorption sites, which results in the sites remaining unsaturated during the adsorption process. It can also be as a result of the decrease in the specific surface area of the adsorbent as a result of the cohesive property of montmorillonite, which results in the coming together of adsorbent particles leading to the blockage of some of the active sites [29].

**Equilibrium isotherm analysis**

In order to effectively analyze and design an adsorption process it is important to understand the equilibrium isotherm application. Adsorption isotherms provide basic physicochemical data for evaluating the applicability of the adsorption process as a unit operation. In this regard, the Langmuir, Freundlich, Temkin and D–R isotherms were applied to the experimental evaluation. The regression coefficient (R^2) was utilized to determine the best fitted model and the closer the R^2 values to 1, the better the model fit. However, due to the inherent bias resulting from linearization, the mechanistic conclusion from the good fit (R^2) of the models alone should be avoided when deciding the applicability of an isotherm model [32]. Another very important tool for evaluating the applicability of an isotherm model is the non-linear chi-square test (\( \chi^2 \)).

| Isotherm model | Zn(II) | Cu(II) | Mn(II) | Cd(II) | Pb(II) | Ni(II) |
|---------------|--------|--------|--------|--------|--------|--------|
| **Langmuir model** | | | | | | |
| q_L (mg/g) | 5.7 | 1.58 | 0.59 | 0.33 | 0.10 | 0.10 |
| K_L (L/mg) | 0.062 | 0.129 | 0.148 | 0.273 | 0.386 | 1.711 |
| R^2 | 0.639 | 0.971 | 0.987 | 0.772 | 0.548 | 0.099 |
| X^2 | 12.82 | 32.70 | 24.63 | 19.823 | 5.915 | 0.036 |
| **Freundlich model** | | | | | | |
| K_F (L/g) | 0.25 | 0.06 | 0.015 | 0.035 | 0.038 | 0.062 |
| 1/n | 0.642 | 2.435 | 2.958 | 3.387 | 3.260 | 0.460 |
| R^2 | 0.915 | 0.977 | 0.968 | 0.916 | 0.818 | 0.650 |
| X^2 | 0.124 | 0.105 | 0.049 | 0.030 | 0.026 | 0.031 |
| **Temkin model** | | | | | | |
| A (L/g) | 0.381 | 0.359 | 0.324 | 0.536 | 0.762 | 2.998 |
| B (mg/g) | 4.662 | 5.619 | 3.651 | 2.925 | 0.877 | 0.051 |
| R^2 | 0.801 | 0.867 | 0.871 | 0.977 | 0.915 | 0.076 |
| X^2 | 1.006 | 0.426 | 0.175 | 0.133 | 0.023 | 0.028 |
| **D–R model** | | | | | | |
| q_m (mg/g) | 5.601 | 7.652 | 5.613 | 6.653 | 2.149 | 0.101 |
| B (molL^-1J^-1) | 3 \times 10^{-6} | 4 \times 10^{-6} | 6 \times 10^{-6} | 3 \times 10^{-6} | 2 \times 10^{-6} | 2 \times 10^{-7} |
| E (kJ/mol) | 0.408 | 0.353 | 0.288 | 0.408 | 0.5 | 1.581 |
| R^2 | 0.749 | 0.914 | 0.926 | 0.901 | 0.816 | 0.039 |
| X^2 | 0.996 | 0.415 | 0.133 | 0.032 | 0.192 | 0.033 |
The chi-square test is a statistical tool necessary for the best fit of an adsorption model. It is the sum of the squares of the differences between the experimental data and the data obtained by calculating from the models. It is expressed mathematically as:

\[ \chi^2 = \sum \left[ \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{cal}}} \right] \]

where \( q_{\text{exp}} \) (mg/g) is the experimental data of the equilibrium capacity and \( q_{\text{cal}} \) (mg/g) is the equilibrium capacity obtained by calculating from the model. \( \chi^2 \) would be a smaller number if the data from the model are similar to the experimental one and would be a larger number if they are different. The equilibrium isotherm parameters calculated are presented in Table 3. It was observed that the Langmuir isotherm is not applicable to the adsorption process due to the low \( R^2 \) and large \( \chi^2 \) recorded. This suggests that the adsorption process may not be attributed to a monolayer adsorption unto a homogenous adsorbent. The \( R_L \) values obtained for the metal ions at all temperatures were between 0.223 and 0.962, which indicates that the adsorption of the metals unto UMC is a favorable process. The Freundlich model was found to present the best fit among all the isotherms considering the high \( R^2 \) and low \( \chi^2 \) values obtained. The only exception was observed for Pb(II) and Ni(II), where the Temkin isotherm was found to be more applicable. The conformity of the data to the Freundlich model suggests a multilayer adsorption of metal ions unto a heterogeneous surface of UMC. Furthermore, considering the energy obtained from the D–R isotherm for all metal ions, the values are very much less than 8 kJ/mol. This indicates that the metal ions adsorption from the automobile effluent unto UMC is a physical process. A physical adsorption is desirable as the energy barrier to be overcome by metal ions is low and also facilitates easy desorption of metals during regeneration of the adsorbent.

Influence of particle size

The particle size of an adsorbent can have a significant effect on the adsorption capacity of the adsorbent. Therefore it was investigated using adsorbent sizes in the range 100–500 \( \mu \)m. The influence of particle size of UMC on the removal of heavy metals from the automobile effluent at 300 K is shown in Fig. 6. A decrease in the adsorption of all the metal ions with increase in particle size of UMC was recorded. This decrease is attributed to a decrease in the specific surface area of the adsorbent with increase in particle size [31]. The breaking of larger particles helps to open up more sites and channels on the surface of UMC resulting in more accessibility for metal ions owing to better diffusion [33]. An insignificant adsorption of Pb and Ni ions was recorded at larger particle sizes due to the extremely low concentration of these metals in the effluent as stated earlier. Furthermore, it has been reported that smaller particle sizes move faster in the solution compared to larger particles resulting in a faster rate of sorption [34]. For optimum sorption the particle size of 100 \( \mu \)m was chosen and utilized in this study.

Influence of contact time

The time it takes metal ions and adsorbent to reach equilibrium is of considerable importance in adsorption experiment because it depends on the nature of the system used and can provide information on the process mechanism. The effect of contact time on the adsorption of heavy metals from the effluent was studied at temperatures of 300, 313 and 323 K and the results are presented in Fig. 7. It was observed that the rate of removal of metal ions was rapid initially (with the exception of Pb and Ni) and became gradual until an equilibrium time beyond
which there was no significant increase in the rate of removal. The initial rapid uptake is due to the presence of abundant active sites on UMC at this stage which becomes used up with time attaining saturation [29]. Although Pb and Ni ions still had a lower adsorption due to their lower concentrations, Ni reached equilibrium faster (around 90 min) compared to Pb(II) ions which attained equilibrium around 180 min. Similarly, the adsorption of the other metal ions on UMC at all temperatures presented various equilibrium times of 90 min for Cu, 120 min for Zn, 150 min for Mn and around 180 min for Cd ions. This implies that the concentration of the metal ion in solution was not the major determining factor in the rate of adsorption. Also, the solution temperature did not significantly affect the rate of removal although it affected the overall adsorption capacity of UMC for the metals. The different equilibrium times observed for the metal ions may be explained by considering the hydrated ionic radii of the metal ions. The ionic radii of the metals are given as Ni (0.69 Å) < Cu (0.72 Å) < Zn (0.74 Å) < Mn (0.80 Å) < Cd (0.97 Å) < Pb (1.20 Å). This implies that the smaller the ionic radii the faster the rate of adsorption [15]. Although the ionic radii of Cu and Zn are very close, their rates of adsorption were quite different. This might be due to differences in other properties of the metals such as their electronegativity, strength of acidity and the pKOH values of the metal hydroxides in solution [31].

Kinetic model analysis

The ability to predict the rate of adsorption for a given system is one of the most important factors in adsorption system design, as the system kinetics determines adsorbate residence time and the reactor dimensions. In this regard, the pseudo-first order, pseudo second order, intraparticle diffusion and liquid film diffusion rate equations were used to analyze the kinetic data. The calculated constants obtained from these models are given in Table 4. It was observed from the linear regression coefficient ($R^2$) values that the adsorption process showed a greater conformity to the pseudo-second order model than the pseudo-first order model. The opposite was observed for Pb and Ni ions. Similarly, the $\chi^2$ values of the pseudo second order model showed good agreement between the experimental qe values and the calculated ones than the first order model, as the values for the former were lower. A reverse trend was also obtained again for Pb. It has been observed that adsorption unto a multi-metal ion system is a complex one. The behavior of each metal ion in a multi-metal ion system depends strongly on the concentration as well as the physical and chemical properties of the adsorbate and adsorbent [33]. We could conclude that the pseudo second order model best represents the kinetics of adsorption for Zn, Cu, Mn and Cd while the pseudo first order became more applicable for the lower concentrations of Pb and Ni ions. Many researchers have obtained the best fit for kinetic data with the pseudo second order model [35].

The pseudo-first order and pseudo-second order models could not identify the diffusion mechanism therefore the kinetic result was further analyzed with the intraparticle diffusion model and the liquid film diffusion model. The adsorption mechanism is usually controlled by the film diffusion or intraparticle diffusion or both [36]. From Table 4, the low $R^2$ values presented by the intraparticle diffusion model suggest that the intraparticle diffusion mechanism did not play a major role in the overall sorption of the metal ions at all temperatures. Also, the occurrence of the intercepts ($C \neq 0$) indicates the involvement of surface phenomenon. This was supported by the good $R^2$ values presented by the film diffusion model. This revealed very important information that the rate controlling mechanism of adsorption is external liquid surface layer diffusion, although it was not the sole rate controlling mechanism due to the occurrence of the intercept ($Y$).

Thermodynamic analysis

The determination of thermodynamic parameters (ΔΗ°, ΔS°, and ΔG°) is important to evaluate the feasibility, spontaneity and heat change of the adsorption process. The calculated val-

| Model/metals | Zn(II) | Cu(II) | Mn(II) | Cd(II) | Pb(II) | Ni(II) |
|--------------|--------|--------|--------|--------|--------|--------|
| Pseudo-first order model | | | | | | |
| $q_e$ (mg/g) | 9.616 | 12.11 | 3.39 | 2.64 | 0.61 | 0.51 |
| $K_1$ (min$^{-1}$) | 0.025 | 0.041 | 0.021 | 0.018 | 0.005 | 0.018 |
| $R^2$ | 0.934 | 0.945 | 0.970 | 0.917 | 0.5 | 0.931 |
| $\chi^2$ | 10.843 | 15.678 | 21.27 | 15.916 | 0.689 | 2.19 |
| Pseudo-second order model | | | | | | |
| $q_e$ (mg/g) | 7.09 | 5.0 | 2.93 | 2.39 | 0.04 | 0.52 |
| $h$ (mg/g min) | 0.148 | 0.162 | 0.038 | 0.018 | 0.0001 | 0.0007 |
| $K_2$ (g/mg min) | 0.003 | 0.006 | 0.004 | 0.003 | 0.072 | 0.003 |
| $R^2$ | 0.952 | 0.965 | 0.927 | 0.953 | 0.208 | 0.044 |
| $\chi^2$ | 0.475 | 0.396 | 0.154 | 0.032 | 27.448 | 0.135 |
| Intraparticle diffusion model | | | | | | |
| $K_d$ (mg/g min$^{-1/2}$) | 0.319 | 0.204 | 0.137 | 0.105 | 0.042 | 0.009 |
| $C$ | 1.351 | 1.566 | 0.217 | 0.074 | 0.306 | 0.013 |
| $R^2$ | 0.675 | 0.589 | 0.759 | 0.808 | 0.730 | 0.580 |
| Film diffusion model | | | | | | |
| $K_{f}$ (mg/g min) | 0.04 | 0.039 | 0.023 | 0.018 | 0.006 | 0.18 |
| $Y$ | 1.17 | 0.8 | 0.566 | 0.544 | 0.376 | 0.72 |
| $R^2$ | 0.919 | 0.963 | 0.976 | 0.922 | 0.911 | 0.833 |
values obtained at adsorbent doses of 0.1–0.5 g are given in Table 5. An exothermic adsorption process was indicated at doses of 0.1 and 0.2 g for Zn, Cu, Mn and Cd while an endothermic adsorption was obtained at higher doses of 0.3–0.5 g. The adsorption of Pb and Ni was found to be endothermic at all doses (0.1–0.5 g). The exothermic adsorption recorded for some of the metals is simply due to higher concentration and the existence of limited number of active sites due to smaller adsorbent doses. Therefore as the temperature increases the adsorbed metal ions on the saturated surface of UMC acquires more kinetic energy for desorption into the bulk phase [37]. On the other hand, at higher doses which present active sites, the acquired kinetic energy is utilized for the movement of the metal ions to the unsaturated active sites. Pb and Ni are present in lower concentrations, so increase in temperature enhances their movement to the surface of UMC (due to higher kinetic energy) in a competitive system where metals with higher concentration are present. This result was corroborated with the $\Delta S^0$ values being negative at lower doses of 0.1–0.2 g for Zn, Cu, Mn, and Cd, indicating a decrease in randomness at the solid-solution interface [37], and also the positive values for Pb and Ni indicating an increase in randomness at the interface [29]. A feasible and spontaneous process was observed at all temperatures for Zn, Cu, Mn and Cd as negative $\Delta G^0$ values were obtained. A more complex situation was observed for Pb and Ni in which a non-spontaneous process accounted for some of the adsorptions due to the positive $\Delta G^0$ values. This might be due to the very low concentration of these metals as stated earlier. However, the energy acquired by the metals with increase in temperature and increase in the number of active sites with adsorbent dose tend to make the process spontaneous. This supports our discussion on the $\Delta H^0$ and $\Delta S^0$ values obtained.

### Conclusions

The adsorption of heavy metals from an automobile effluent on a montmorillonite as a low cost adsorbent was carried out using batch sorption technique. The montmorillonite proved to be suitable for significant removal of all the metals ions from the effluent despite been used in its unmodified form. This adsorbent which is present in abundant amount in Eastern Nigeria can be utilized for treatment of effluents containing high concentration of heavy metals thereby reducing the toxic effects posed by these metals to the environment.

| Parameter/adsorbent dose | 0.1 g | 0.2 g | 0.3 g | 0.4 g | 0.5 g |
|--------------------------|-------|-------|-------|-------|-------|
| Zn(II)                   |       |       |       |       |       |
| $\Delta H^0$ (kJ/mol)    | −4.55 | −2.72 | 3.97  | 10.39 | 8.28  |
| $\Delta S^0$ (J/mol K)   | −10.97| −2.09 | 21.57 | 44.83 | 40.88 |
| $\Delta G^0$ (kJ/mol)    | −1.097| −1.995| −2.494| −3.117| −4.05 |
| Cu(II)                   |       |       |       |       |       |
| $\Delta H^0$ (kJ/mol)    | −5.36 | −3.76 | 4.94  | 7.98  | 9.16  |
| $\Delta S^0$ (J/mol K)   | −13.58| −6.38 | 24.47 | 35.35 | 40.95 |
| $\Delta G^0$ (kJ/mol)    | −1.147| −1.745| −2.419| −2.669| −3.142|
| Mn(II)                   |       |       |       |       |       |
| $\Delta H^0$ (kJ/mol)    | −6.25 | −1.01 | 10.64 | 10.37 | 13.54 |
| $\Delta S^0$ (J/mol K)   | −21.28| −2.44 | 37.85 | 37.93 | 50.02 |
| $\Delta G^0$ (kJ/mol)    | −0.399| −0.199| −0.723| −1.144| −1.471|
| Cd(II)                   |       |       |       |       |       |
| $\Delta H^0$ (kJ/mol)    | −9.96 | −3.33 | 26.21 | 36.06 | 39.18 |
| $\Delta S^0$ (J/mol K)   | −32.05| −7.28 | 57.99 | 124.04| 135.60|
| $\Delta G^0$ (kJ/mol)    | −0.074| −0.897| −1.222| −1.222| −1.596|
| Pb(II)                   |       |       |       |       |       |
| $\Delta H^0$ (kJ/mol)    | 28.16 | 24.12 | 24.19 | 24.19 | 35.57 |
| $\Delta S^0$ (J/mol K)   | 76.09 | 78.98 | 78.98 | 117.06| 119.95|
| $\Delta G^0$ (kJ/mol)    | 2.369 | 1.917 | 0.474 | 0.474 | 0.474 |
| Ni(II)                   |       |       |       |       |       |
| $\Delta H^0$ (kJ/mol)    | 45.58 | 65.45 | 48.83 | 75.86 | 66.60 |
| $\Delta S^0$ (J/mol K)   | 136.27| 201.03| 152.15| 241.11| 214.92|
| $\Delta G^0$ (kJ/mol)    | 5.013 | 5.013 | 2.544 | 3.218 | 1.397 |
| $\Delta S^0$ (kJ/mol)    | 2.029 | 2.654 | 2.654 | 0.988 | 0.937 |
| $\Delta G^0$ (kJ/mol)    | 2.095 | 0.429 | −1.182| −2.363| −3.786|
Sorption of heavy metals on montmorillonite

Conflict of Interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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