Studies on the Performance of Shale and Bentonite for the Removal Cr$^{3+}$ and Mn$^{2+}$ ions from Wastewater using Batch Experimental Techniques and Inferential Statistics

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Abstract
To investigate the performance of locally available shale for the treatment of wastewater containing chromium and manganese, six different adsorbents were prepared from shale and bentonite, namely; raw shale (RSA), raw bentonite (RBA), calcinated shale (CSA), calcinated bentonite (CBA), acid activated shale (AAS) and acid activated bentonite (AAB). The textural characteristics and chemical composition of the adsorbents were determined using scanning electron microscopy (SEM) and X-Ray fluorescence (XRF). The effects of selected adsorption variables such as initial metal ion concentration, adsorbent dose, pH, and contact time on the sorption of Cr$^{3+}$ and Mn$^{2+}$ ions were studied using batch adsorption techniques while inferential statistics was employed to select the best adsorbent for specific metal ion removal. Result of the microstructural analysis using SEM revealed that the surface characteristics of the shale and bentonite materials changes drastically with calcination and acid treatment with the acid treated shale and bentonite showing a better irregular porous surface structure. XRF analysis revealed that aluminum oxide and silicon oxide are the dominant oxides present in both shale and bentonite. Inferential statistical analysis revealed that acid activated shale was the most suitable adsorbent for the removal of manganese while acid activated bentonite was the best for chromium ion removal.

Keywords: Calcination, acid activation, inferential statistics, SEM and XRF

DOI: 10.7176/JEES/9-10-14
Publication date: October 31st 2019

1. Introduction
Recently, adequate attention has been given to environmental pollution resulting from the discharge of untreated effluents containing toxic heavy metals into water bodies. Heavy metals even in trace amount can be dangerous to plants and animal including human being since they are not susceptible to biological degradation like other organic pollutants. Some conventional processes have been developed over the years to remove these heavy metals from water and wastewater they include; solvent extraction, chemical precipitation, ion exchange process, electrolytic precipitation, and reverse osmosis (Ong et al., 2007). However, these physicochemical processes possess significant limitations of being highly expensive, sophisticated and environmentally disruptive, requiring the input of external chemical additives or energy. In addition, some of these conventional processes especially electrolytic and chemical precipitation generate concentrated sludge or other kind of waste that must be properly disposed to avoid further damage to the environment (Lin and Juang, 2002). Attempts have been made by several researchers to develop inexpensive alternative methods for heavy metal removal. Adsorption is an alternative technology for metal separation from aqueous solution and with the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants including heavy metals (Weng et al., 2007). In this research, shale and bentonite, both in raw form, calcinated form and acid activated form, were employed as adsorbents for the treatment of wastewater containing chromium (III) and manganese (II) ions. Shale and bentonite are members of the clay family. They are naturally occurring minerals and locally available. The adsorption capacities of clay minerals result from a net negative charge on the structure. This negative charge gives clay minerals the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity (Ilaboya, 2017).

2. Materials and Methods
2.1 Equipment used for the experiment
Major equipment used in this study is presented in Table 1. Minor equipment includes: pH meter, digital weighing balance and hand held conductivity meter while the glass wares include: reagent bottles, conical flask, measuring cylinder, glass funnels and beakers.
Table 1: Equipment Details

| S/No | Equipment Name                  | Location                        | Model            |
|------|---------------------------------|---------------------------------|------------------|
| 1    | Laboratory Oven                 | Civil Engineering Lab (UNIBEN)  | DHG 9101-2A      |
| 2    | Industrial Furnace              | Engineering Workshop (UNIBEN)   | DHG 9101-5A      |
| 3    | Constant Temperature Water Bath| Civil Engineering Lab (UNIBEN)  | DHG 3101-6A      |
| 4    | Hot Plate with Magnetic Stirrer | Civil Engineering Lab (UNIBEN)  | HJ-3D            |
| 5    | Scanning Electron Microscope    | Department of Chemistry         | APEX 3020 PSEM 2 |
|      | (SEM)                           | (Kwara State University)        |                  |
| 6    | Fourier Transform Infra-red    | Cherish Environmental Lab        | FTIR 2000, Shimadzu Kyoto, Japan |
|      | (FTIR)                          | (IBADAN)                        |                  |
| 7    | X-Ray Fluorescence             | Cherish Environmental Lab        | APEX 3022        |
|      | (XRF)                           | (IBADAN)                        |                  |
| 8    | Atomic Absorption Spectrophotometer | Martlet Engineering Lab (Benin City) | UNICAM SOLAR 969 |

2.2 Collection and preparation of adsorbent

Shale was collected from its deposit at Okada the administrative headquarter of Ovia North East Local Government Area of Edo State, Nigeria. First, it was soaked in a plastic containing 5% hydrogen peroxide to remove any carbonaceous matter that can interfere with the metal adsorption capacity of the shale. Thereafter, it was washed with distilled water to remove any water-soluble impurities before being dried in hot air oven at 50-70°C for 8 hours. The dried shale was then reduced to fine and sieved using sieve size of 212µm before use (Maria das et al., 2012).

For calcination, 500g of the dried sieved shale was placed in a furnace at a temperature of 550°C for 10 hours. For acid activation, 200g of the calcinated shale was mixed with 1 liter 0.25M sulphuric acid, the mixture was heated at 105°C for 30 minutes. After slow cooling, the slurry was filtered and washed free of acid using distilled water as indicated by a pH meter. The shale was dried at a temperature of 100°C for 30 – 45 minutes, ground using mortar and pestle, sieved to 212 µm and stored in a desiccator to cool before use (Krishna et al., 2006). The same procedure was adopted in preparing the adsorbent from bentonite. In all, a total of six (6) adsorbents were prepared for this research and they are; acid activated shale (AAS), acid activated bentonite (AAB), calcinated shale (CSA), calcinated bentonite (CBA), raw shale (RSA) and raw bentonite (RBA).

2.3. Characterization of adsorbent

2.3.1. Analysis of microstructures

The microstructural arrangement and morphology of shale and bentonite were analyzed using scanning electron microscopy (APEX 3020 PSEM 2) to give adequate information about their topological presentations. Such presentations may provide possible explanations for the solid behaviour (Omisanya et al., 2012).

2.3.2. Chemical composition

The chemical composition of shale and bentonite was studied using X-Ray Fluorescence (XRF) APEX 3022 after digestion. Chemical digestion of the solid adsorbent was done as follows: (1:1) mixture of 0.25M solution of hydrochloric acid and Nitric acid was prepared. A mixture of (1:10) of the solid adsorbent to acid solution was obtained and stir for 30 minutes. The solution was filtered and the filtrate was used for the analysis (Omokhaye, 1999).

2.4. Preparation of adsorbate solution

All the chemicals used in this research are analytical grade. Stock solution of chromium and manganese were prepared by dissolving accurate quantities of manganese (II) chloride tetrahydrate (MnCl₂・4H₂O), and chromium (III) hydroxide [Cr₂(OH)₃] in one liter of distilled water. All working solutions were obtained by diluting the stock solution with distilled water and the concentration of metal ion present in solution was determined by Atomic Absorption Spectrophotometer (AAS). A duplicate was analyzed for each sample to track experimental error and show capability of reproducing results. The pH of the solution was adjusted to the desired values for each experiment with drop wise addition of 1M HNO₃ or 1M NaOH according to (Dawodu et al., 2012, Hao and Wang, 2007, Chih et al., 2007).
2.5. Adsorption studies
Adsorption study was carried out to determine the effect of pH, adsorbent dose, contact time and initial metal ion concentration using batch adsorption technique. The adsorption experiment was performed at different variable range as follows; pH (2, 4, 6, 8, and 10), adsorbent dose (0.2, 0.4, 0.6, 0.8 and 1.0g), contact time (20, 40, 60, 80, 100, and 120 minutes and varied initial metal ion concentration. A 250ml conical flask containing the adsorbent and 50ml wastewater was agitated at 150rpm using a mantle fitted with magnetic stirrer. The pH value of the solution was kept at the optimum for each heavy metal. The separation of the adsorbent from wastewater was carried out by filtration with 150mm whatman filter paper and the filtrates were stored in sample cans in a refrigerator prior to analysis. The residual metal ion concentration was determined using Atomic Absorption Spectrophotometer (AAS). The amount of heavy metal ions removed during the series of batch investigation was determined using the mass balance equation of the form; (Badmus et al, 2007).

\[ q = \frac{V}{m} \left[ C_0 - C_e \right] \]  

(1)

Where: q, defines the metal uptake (mg/g); C₀ and Cₑ: are the initial and equilibrium metal ion concentrations in the aqueous solution [mg/l] respectively; V: is the aqueous sample volume (ml) and m: is the mass of adsorbent used (g). The efficiency of metal ion removal (%) was calculated using the mass balance equation of the form (Gimbert et al., 2008, Gunay et al., 2007, Hong et al., 2009).

Efficiency (%) = \left( \frac{C_0 - C_e}{C_0} \times 100 \right) \]  

(2)

Where: C₀ and Cₑ are the metal ion concentrations (mg/l) in aqueous solution before and after adsorption respectively.

2.6 Optimum pH determination
pH was adjusted in the range from 2-10 by drop wise addition of 1M HNO₃ or 1M NaOH to Cr³⁺ and Mn²⁺ ion solution. Batch adsorption experiment was conducted at various pH by adding 1.0g of adsorbents to 50ml solutions of metal ions inside conical flasks and mixed on a mantle fitted with magnetic stirrer at 150 rpm for 120 minutes at 27±2°C. The initial metal ion concentrations of Cr³⁺ and Mn²⁺ in the solution were varied from 10, 20, 30, 40, 50 and 60mg/l for Cr³⁺ and 4, 8, 12, 16, 20, 24mg/l for Mn²⁺ ion with pH ranging from 2 to 10. The adsorbent was separated from wastewater by filtering with 150mm whatman filter paper and the residual metal ion concentration was determined using Atomic Absorption Spectrophotometer (AAS).

3. Results and discussion
Scanning electron micrograph of raw shale, calcinated shale, acid activated shale, raw bentonite, calcinated bentonite, and acid activated bentonite are presented in Figures 1, 2 and 3.

Figure 1: SEM of raw shale (a) and raw bentonite (b)
Figure 2: SEM of calcinated shale (c) and calcinated bentonite(d)

Figure 3: SEM of acid activated shale (e) and acid activated bentonite (f)

Scanning electron micrograph was taken to verify the presence of micropores in the structure of shale and bentonite fraction. Significant morphological differences were observed between the shale and bentonite samples with the shale samples exhibiting better irregular and porous surface characteristics of different lamellae sizes. Chemical analysis of shale and bentonite fractions conducted using X-Ray Fluorescence (XRF) are presented in Figures 4 and 5.
It was observed from the result of Figure 4 and 5 that aluminum oxide and silicon oxide were the dominant oxides present in both shale and bentonite with shale having higher percentage by weight of both oxides. Figures 6 and 7 shows the graphical variation between the sorption efficiency (%) and the pH of wastewater containing Cr$^{3+}$ and Mn$^{2+}$
The removal of metal ions from wastewater by adsorption is related to the pH of the solution. pH affects the surface charge of adsorbents, the degree of ionization, and the species of adsorbate. Maximum adsorption of Cr$^{3+}$ and Mn$^{2+}$ ions onto shale and bentonite was observed at pH of 6 and 8 as indicated by the optimum line on the graph after which adsorption again decrease as the pH of the solution increases. From the results of Figures 6 and 7, it was observed that acid activated shale (AAS) had the highest removal efficiency for Cr$^{3+}$ and Mn$^{2+}$ ions followed by acid activated bentonite (AAB) thereafter calcinated shale (CSA), calcinated bentonite (CBA), raw shale (RSA) and finally raw bentonite (RBA) given in that order (AAS > AAB > CSA > CBA > RSA > RBA). For Cr$^{3+}$ ion, adsorption reaches a maximum of 72.8%, at pH of 6 using acid activated shale while for Mn$^{2+}$ ion, adsorption reaches a maximum of 87.3%, at pH of 8 using acid activated shale. Decrease in the adsorption efficiency of Cr$^{3+}$ and Mn$^{2+}$ ions observed at lower pH for all the adsorbent used could be ascribed to the hydrogen ions or hydroxonium ions (H$^+$ or H$_3$O$^+$) competing with Cr$^{3+}$ and Mn$^{2+}$ for sorption sites. This means that, at higher H$^+$ or H$_3$O$^+$ ion concentration emanating from lower pH, the adsorbent surface becomes more positively charge thus, creating some kind of repulsive forces which reduces the attraction between the adsorbents and the metal ions. In which case, the metal ions are prevented from approaching the binding sites on the adsorbents thus resulting to a decrease in the percentage metal ions removal as established in a research conducted by (Abd EL-Latif and Amal, 2009; McKay et a., 1985). In contrast, as the pH increases from 2 to 8, there was a corresponding increase in deprotonation of the adsorbent surface, thus leading to a decrease in hydrogen ion concentration occasioned by the production of more hydroxyl (OH$^-$) ions on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favour adsorption of positively charge species on the adsorbent surface. The increase in metal uptake as pH increases can be explained on the basis of a decrease in competition between hydroxonium ions and metal species for the surface sites and also by decrease in positive surface charge on the adsorbent, which result in a lower electrostatic repulsive force between the surface and the metal ion and hence uptake of metal ions.
increases (Low et al., 1993). Figures 8 and 9 shows the graphical variation between the sorption efficiency (%) and adsorbent dose.

![Figure 8: Influence of adsorbent dose on sorption of Cr\(^{3+}\) ions on adsorbents prepared from shale and bentonite](image1)

![Figure 9: Influence of adsorbent dose on adsorption of Mn\(^{2+}\) ions on adsorbents prepared from shale and bentonite](image2)

The percentage removal of metal ions increases as the dose of adsorbents increases reaching a maximum of 72.8%, 66.5%, 61.4%, 58.4%, 56.3% and 55.1% for Cr\(^{3+}\) ion adsorption and 87.3%, 82.3%, 73.1%, 69.4%, 63.6%, 62.7% for Mn\(^{2+}\) ion adsorption. It was observed from the results that acid activated shale had the highest removal efficiency followed by acid activated bentonite. The increase in metal ion adsorption with increasing dose of adsorbent as observed in Figures 8 and 9 for all the adsorbent used may be due to the increase in availability of surface-active sites resulting from the increased dose of the adsorbents (Garg et al., 2003; Saeed et al., 2005). Percentage of adsorption normally increased with increase in adsorbent dosage but the amount adsorbed per unit mass of the adsorbent decreased considerably as the dose of adsorbent increases as observed in Figures 10 and 11.
Figure 10: Influence of adsorbent dose on the amount of Cr$^{3+}$ ions adsorbed.

Figure 11: Influence of adsorbent dose on the amount of Mn$^{2+}$ ions adsorbed.

The decrease in unit adsorption with increasing dose of adsorbent was basically due to adsorption sites remaining unsaturated during the adsorption reaction. Figures 12 and 13 shows the graphical variation between the sorption efficiency (%) and contact time.
Contact time is a very important factor that affects the sorption of metal ion. It was observed from the results of Figures 12 and 13 that the efficiency of Cr$^{3+}$ and Mn$^{2+}$ ion removal increases steadily with time and reached a steady state at 100 minutes of contact. Although, there was similarity in the sorption mechanism of the metal ions studied, it was observed that the adsorbent used shows superior affinity to Mn$^{2+}$ ions as observed in Figure 13. At equilibrium, removal efficiency of Mn$^{2+}$ ion was observed to be 87.3% while that of Cr$^{3+}$ ion was 72.8%. Acid activated shale was observed to have the best performance in terms of metal ion removal followed by acid activated bentonite and calcinated shale with raw bentonite having the least performance. The performance of acid activated shale in the removal of metal ion from wastewater was due to its cation exchange capacity coupled with the high surface area. A sharp increase in adsorption was noticed in the first twenty minutes of experimentation as observed in Figures 12 and 13 and thereafter, adsorption rate begins to increase steadily up to 100 minutes of contact time and then flattens out signifying that equilibrium point has been reached. The increased rate of adsorption noticed at the early stage of experimentation was traced to the availability of abundant active sites on the adsorbent surface which gradually became occupied by the metal ion with time. With increasing contact time, the adsorbent active sites get progressively filled by the metal ion with fewer active sites remaining leading to gradual reduction in sorption rate (Johnson, 1990). The mechanism of adsorption that defines the early stage of adsorption contact time was ion exchange which was occasioned by the attractive force between the negative ions present in the active...
sites of the adsorbent and the positive metal ions. Ion exchange is a diffusion mechanism which normally occurs at the early stage of the adsorption process and result in fast uptake of metal ion as observed in the first twenty minutes of Figures 3.9a and 3.4b respectively. The gradual increase in adsorption after that sharp increase that was noticed at the early stage can be explained by another form of adsorption mechanism known as chemical attachment (Chemisorption) (Low et al., 1993). Figures 14 and 15 shows the graphical variation between the sorption efficiency (%) and initial metal ion concentration.

![Figure 14: Effects of initial metal ion concentration on the adsorption efficiency of Cr$^{3+}$ ions onto adsorbents prepared from shale and bentonite.](image)

![Figure 15: Effects of initial metal ion concentration on the adsorption efficiency of Mn$^{2+}$ ions onto adsorbents prepared from shale and bentonite.](image)

From the result of Figures 14 and 15, it was observed that the efficiency of metal ion removal (%) decreases with increasing metal ion concentration. In Figure 14 for example, efficiency of Cr$^{3+}$ removal decreases from 72.8% to 27.4% for acid activated shale, 66.5% to 29.1% for acid activated bentonite, 61.4% to 26.0% for calcinated shale, 58.4% to 23.4% for calcinated bentonite, 56.3% to 24.3% for raw shale and 55.1% to 23.8% for raw bentonite when initial metal ion concentration changes from 10mg/l to 60mg/l respectively. In Figure 15, efficiency of Mn$^{2+}$ ion removal decreases from 87.3% to 37.3% for acid activated shale, 82.3% to 36.2% for acid activated bentonite, 73.1% to 29.2% for calcinated shale, 69.4% to 28.7% for calcinated bentonite, 63.6% to 24.6% for raw shale and 62.7% to 23.4% for raw bentonite when initial metal ion concentration changes from 4mg/l to 24mg/l respectively. These results are in line with the previous work reported in Krishna and Susmita, 2006; Yu et al., 2003. The decrease in the removal efficiency of metal ion with increasing concentration of the metal ion at fixed adsorbent dose of 1.0g can be explain as follows; the adsorption potential of adsorbent materials is purely dependent on the number of binding sites present at the surface of that adsorbent. More also, a unit mass of an adsorbent material contains a certain number of binding sites. At low initial metal ion concentration, the amount of metal ion present in the bulk solution is small compare to the number of binding sites on the adsorbent surface making the ratio of absorbable metal ion to the adsorbent binding sites to be small thus making adsorption to be independent of the initial metal ion concentration. The implication is that adsorption is at the apex meaning high rate of adsorption (Krishna and Susmita, 2006). With increasing metal ion concentration, the ratio of absorbable
metal ion to the adsorbent binding sites becomes very large resulting to increased competition for the binding sites. Since there are more adsorbate compare to the available binding sites, a decrease in percentage adsorption will occur due to high adsorbate concentration (Ucun et al., 2003). However, unit mass of the adsorbent is now exposed to a larger number of metal ions owing to high initial metal ion concentration, resulting in an increased metal ion uptake \((q)\) per unit mass of adsorbent (Krishna and Susmita, 2006) as shown in Figures 16 and 17.

![Figure 16: Effects of initial metal ion concentration on the uptake of Cr\(^{3+}\) ion by unit mass of adsorbents prepared from shale and bentonite](image16.png)

![Figure 17: Effects of initial metal ion concentration on the uptake of Mn\(^{2+}\) ion by unit mass of adsorbents prepared from shale and bentonite](image17.png)

To select the most suitable adsorbent for a specific metal ion removal, inferential statistics was employed. Descriptive statistics such as mean, median, modes, standard deviation, range, frequency and percentage are normally employed to give suitable summary information about variables in data sets as presented in Table 2 and 3.
One of the basic limitations of descriptive statistics is that the summary information provided can sometimes be inconclusive especially in practice and decision making (Dwayne, 2010). In this case, such decision refers to the selection of the best adsorbent for a specific metal ion removal. Inferential statistics was therefore chosen for this task since it can provide better understanding and exposure to the hidden information from descriptive statistics. To apply inferential statistics, we required a single categorical variable which is the independent variable and various numerical variables which is the dependent variable. For this problem, the types of adsorbent was used as the independent variable (categorical) while the computed efficiency of metal ion removal was used as the dependent variable (numerical). To test the assumption of differential performance, the following hypothesis were formulated

**H0:** There is no significant difference in the performance of the adsorbents  
**H1:** There is a significant difference in the performance of the adsorbents  

The analysis was performed at 95% confidence interval, which represent 0.05 degree of freedom that is \( p = 0.05 \). For \( P > 0.05 \), the null hypothesis was rejected and it was concluded that there is a significant difference in the performance of the adsorbents. To test the assumption of equal variance, test of homogeneity of variance as presented in Table 4 was employed

| Table 2: Statistics of Cr\(^{3+}\) ion removal |
|---------------------------------------------|
| **Efficiency of Cr\(^{3+}\) Ion Removal (%)** |
| **N** | **Mean** | **Std. Deviation** | **Std. Error** | **95% Confidence Interval for Mean** |
|-------|----------|-------------------|----------------|-------------------------------------|
| AAS   | 6        | 43.817            | 18.2024        | 7.4311                              |
| CSA   | 6        | 40.233            | 13.9308        | 5.6872                              |
| RSA   | 6        | 40.000            | 12.6533        | 5.2882                              |
| AAB   | 6        | 46.450            | 15.3740        | 5.6764                              |
| CBA   | 6        | 39.763            | 13.7616        | 5.5237                              |
| RBA   | 6        | 27.893            | 12.3999        | 5.0618                              |
| Total | 36       | 37.634            | 15.2289        | 5.2381                              |

| Table 3: Statistics of Mn\(^{2+}\) ion removal |
|-----------------------------------------------|
| **Efficiency of Mn\(^{2+}\) Ion Removal (%)** |
| **N** | **Mean** | **Std. Deviation** | **Std. Error** | **95% Confidence Interval for Mean** |
|-------|----------|-------------------|----------------|-------------------------------------|
| AAS   | 6        | 60.817            | 19.6308        | 7.6091                              |
| CSA   | 6        | 48.467            | 16.7240        | 6.8275                              |
| RSA   | 6        | 30.933            | 14.8371        | 6.0817                              |
| AAB   | 6        | 58.233            | 17.6892        | 7.2257                              |
| CBA   | 6        | 45.917            | 15.5925        | 6.3656                              |
| RBA   | 6        | 30.167            | 14.9307        | 6.1159                              |
| Total | 36       | 45.739            | 19.5670        | 3.2612                              |

One of the basic limitations of descriptive statistics is that the summary information provided can sometimes be inconclusive especially in practice and decision making (Dwayne, 2010). In this case, such decision refers to the selection of the best adsorbent for a specific metal ion removal. Inferential statistics was therefore chosen for this task since it can provide better understanding and exposure to the hidden information from descriptive statistics. To apply inferential statistics, we required a single categorical variable which is the independent variable and various numerical variables which is the dependent variable. For this problem, the types of adsorbent was used as the independent variable (categorical) while the computed efficiency of metal ion removal was used as the dependent variable (numerical). To test the assumption of differential performance, the following hypothesis were formulated

**H0:** There is no significant difference in the performance of the adsorbents  
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The analysis was performed at 95% confidence interval, which represent 0.05 degree of freedom that is \( p = 0.05 \). For \( P > 0.05 \), the null hypothesis was rejected and it was concluded that there is a significant difference in the performance of the adsorbents. To test the assumption of equal variance, test of homogeneity of variance as presented in Table 4 was employed

| Table 4: Equal variance assumption |
|-----------------------------------|
| **Test of Homogeneity of variance** |
| **Efficiency of Cr\(^{3+}\) Removal** | Levene statistics | df1 | df2 | Sig. |
|-------------------------------------|-------------------|-----|-----|------|
| 0.399                               | 3                 | 30  |     | 0.845|

| **Efficiency of Mn\(^{2+}\) Removal** | Levene statistics | df1 | df2 | Sig. |
|--------------------------------------|-------------------|-----|-----|------|
| 0.177                                | 5                 | 30  |     | 0.969|

Result of Table 4 gave a p-value of 0.845 and 0.969 for Cr\(^{3+}\) and Mn\(^{2+}\) ion removal. For \( P > 0.05 \), the null hypothesis
was rejected and it was concluded that; there is a significant difference in the performance of the adsorbents in terms of Cr\textsuperscript{3+} and Mn\textsuperscript{2+} ion removal. To select the best adsorbent for the removal of Cr\textsuperscript{3+} and Mn\textsuperscript{2+} ion, the mean plot of performance against the selected adsorbent as presented in Figures 18 and 19 were employed.

From the result of Figures 18 and 19, it was observed that acid activated shale was the best adsorbent for the removal of Mn\textsuperscript{2+} while acid activated bentonite was observed to be the best adsorbent followed by acid activated shale for the removal of Cr\textsuperscript{3+} ion from wastewater.

4. Conclusion
The research paper has successfully investigated the performance of adsorbent prepared from shale and bentonite which are locally available. In addition, the effectiveness of inferential statistic as a new method for classifying adsorbents in terms of their performances in removing metal ions from water and wastewater have also been investigated. The simplicity of inferential statistics compared to Dubinin-Radushkevich isotherm model that is commonly used by most researchers will in no doubt guarantee its wide acceptability.

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