

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

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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 (SEM)	Department of Chemistry (Kwara State University)	APEX 3020 PSEM 2
6	Fourier Transform Infra-red (FTIR)	Cherish Environmental Lab (IBADAN)	FTIR 2000, Shimadzu Kyoto, Japan
7	X-Ray Fluorescence (XRF)	Cherish Environmental Lab (IBADAN)	APEX 3022
8	Atomic Absorption Spectrophotometer (AAS)	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 been 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 (Mariadas 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, 200 g 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 ($MnCl_2 \cdot 4H_2O$), and chromium (III) hydroxide [$Cr_2(OH)_3$] 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 HNO_3 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).

$$q = \frac{V}{m} [C_0 - C_e] \quad (1)$$

Where: q, defines the metal uptake (mg/g); C_0 and C_e : 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).

$$\text{Efficiency (\%)} = \left(\frac{C_0 - C_e}{C_0} \times 100 \right) \quad (2)$$

Where: C_0 and C_e 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 HNO_3 or 1M NaOH to Cr^{3+} and Mn^{2+} 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 $27 \pm 2^\circ\text{C}$. The initial metal ion concentrations of Cr^{3+} and Mn^{2+} in the solution were varied from 10, 20, 30, 40, 50 and 60mg/l for Cr^{3+} and 4, 8, 12, 16, 20, 24mg/l for Mn^{2+} 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.

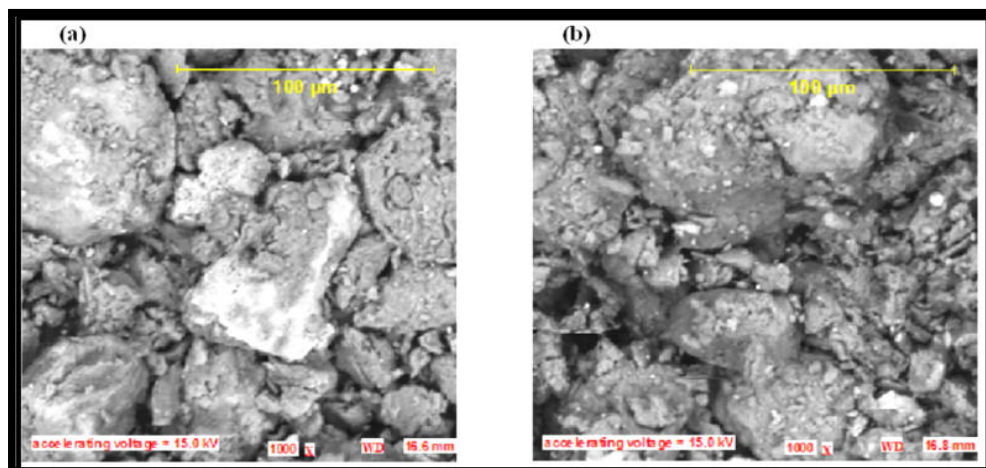


Figure 1: SEM of raw shale (a) and raw bentonite (b)

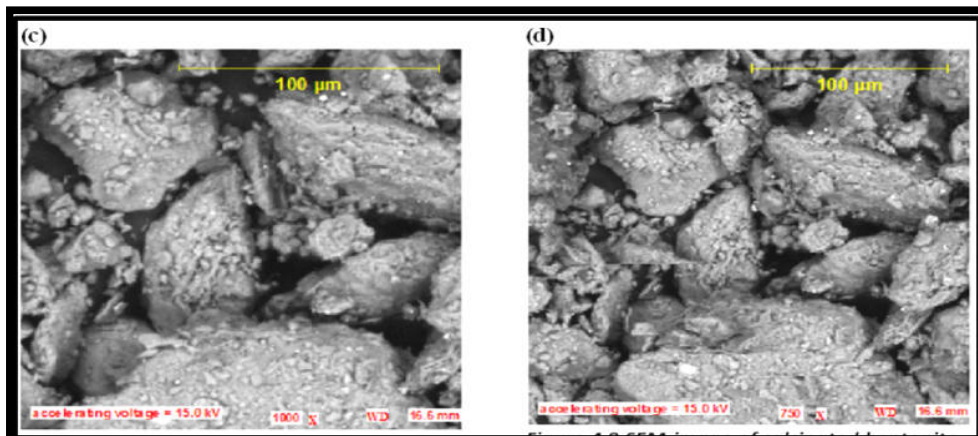


Figure 2: SEM of calcinated shale (c) and calcinated bentonite(d)

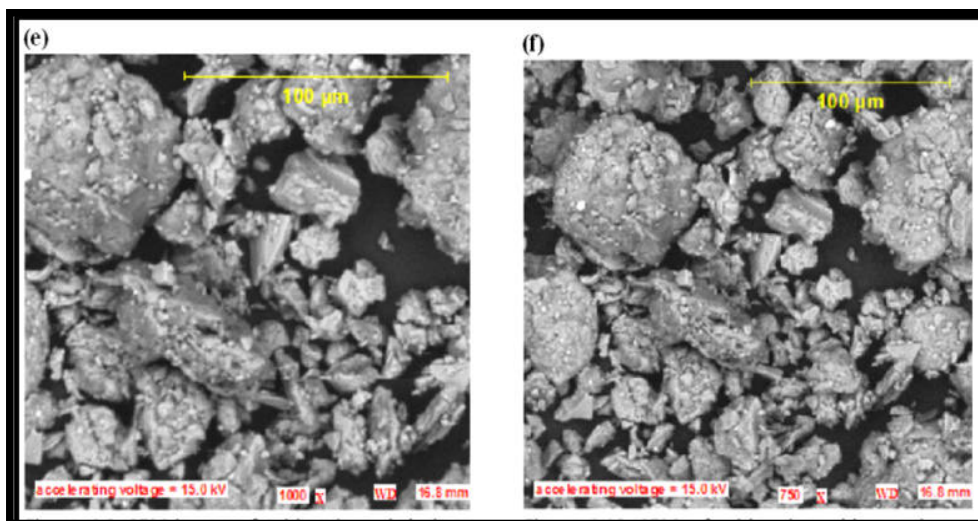


Figure 3: SEM of acid activated shale (e) and acid activated bentonite (f)

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.

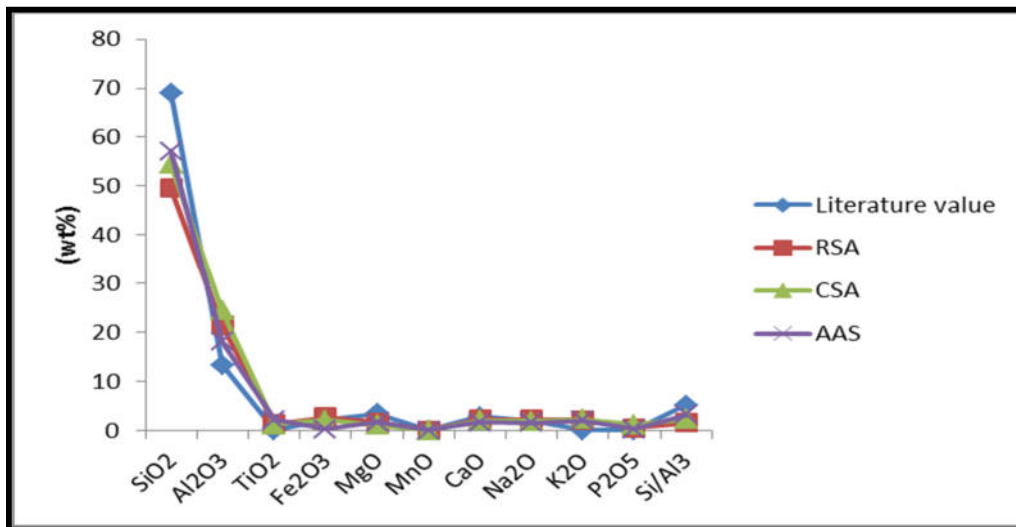


Figure 4: Chemical composition of the different forms of adsorbent from shale

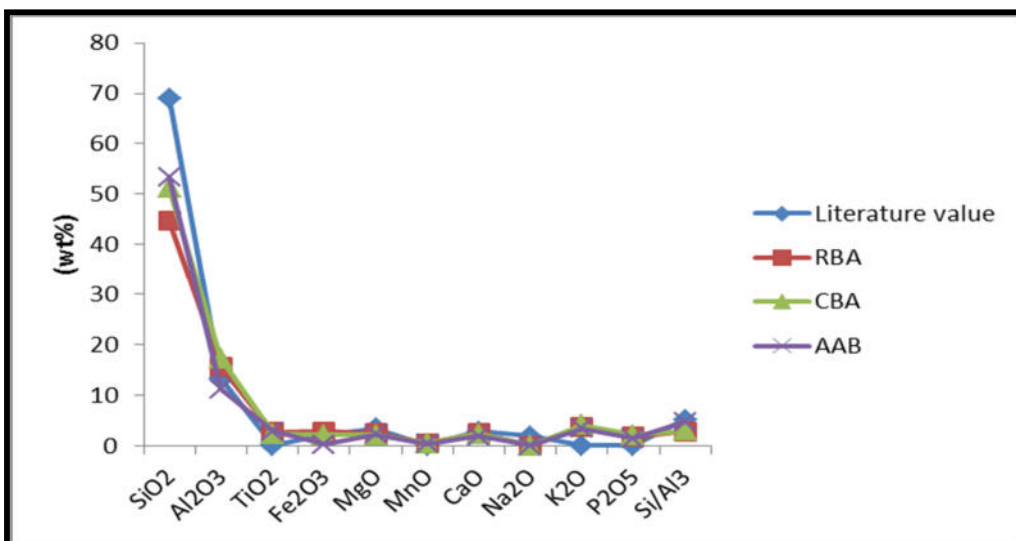


Figure 5: Chemical composition of the different forms of adsorbent from bentonite

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 Cr³⁺ and Mn²⁺

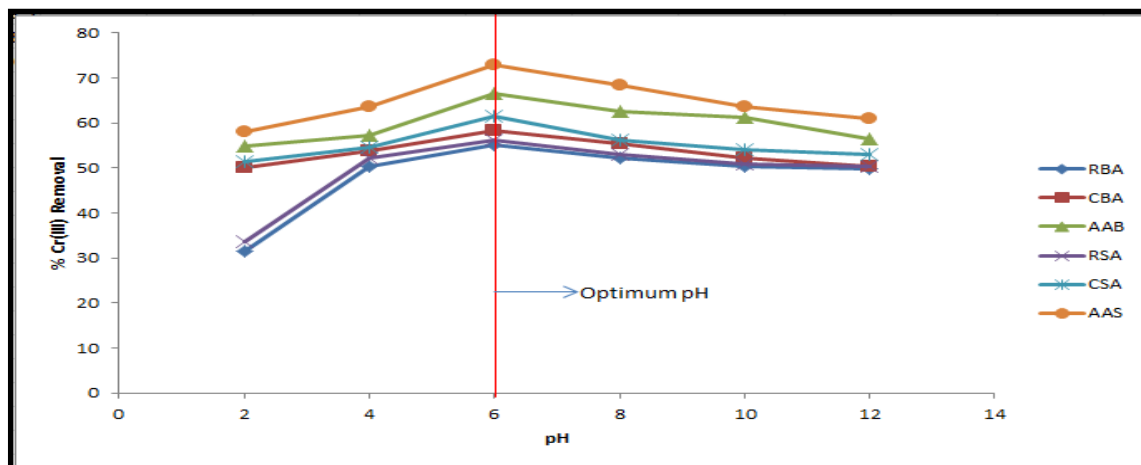


Figure 6: Influence of pH on sorption of Cr³⁺ ions onto shale and bentonite fractions

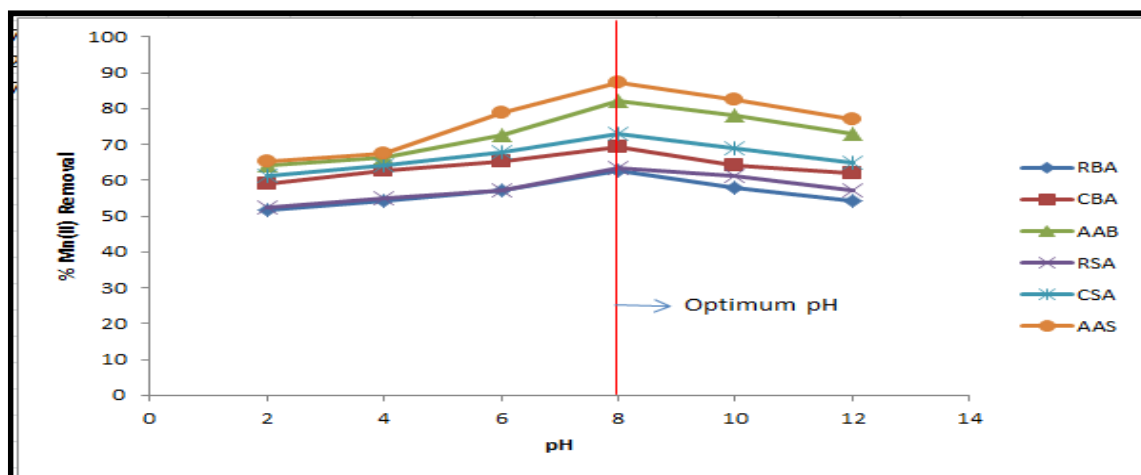


Figure 7: Influence of pH on sorption of Mn²⁺ ions shale and bentonite fractions

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 Cr³⁺ and Mn²⁺ 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 Cr³⁺ and Mn²⁺ 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 Cr³⁺ ion, adsorption reaches a maximum of 72.8%, at pH of 6 using acid activated shale while for Mn²⁺ ion, adsorption reaches a maximum of 87.3%, at pH of 8 using acid activated shale. Decrease in the adsorption efficiency of Cr³⁺ and Mn²⁺ ions observed at lower pH for all the adsorbent used could be ascribed to the hydrogen ions or hydroxonium ions (H⁺ or H₃O⁺) competing with Cr³⁺ and Mn²⁺ for sorption sites. This means that, at higher H⁺ or H₃O⁺ 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 al., 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.

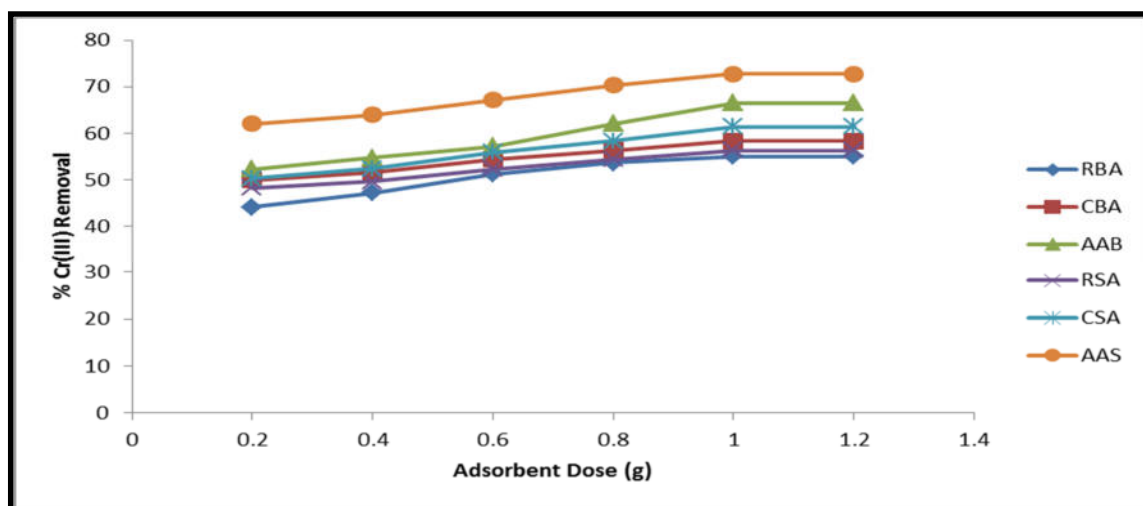


Figure 8: Influence of adsorbent dose on sorption of Cr^{3+} ions on adsorbents prepared from shale and bentonite

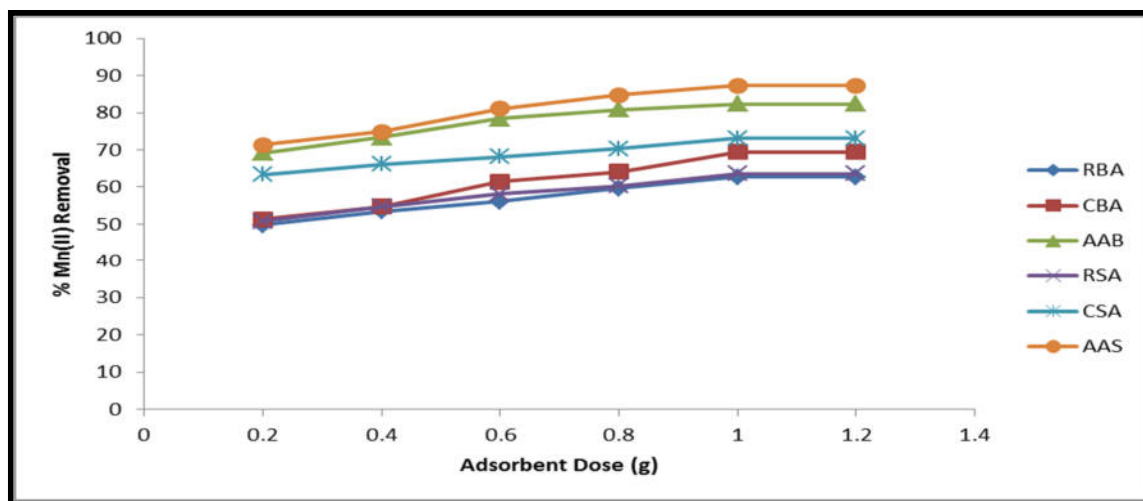


Figure 9: Influence of adsorbent dose on adsorption of Mn^{2+} ions on adsorbents prepared from shale and bentonite

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

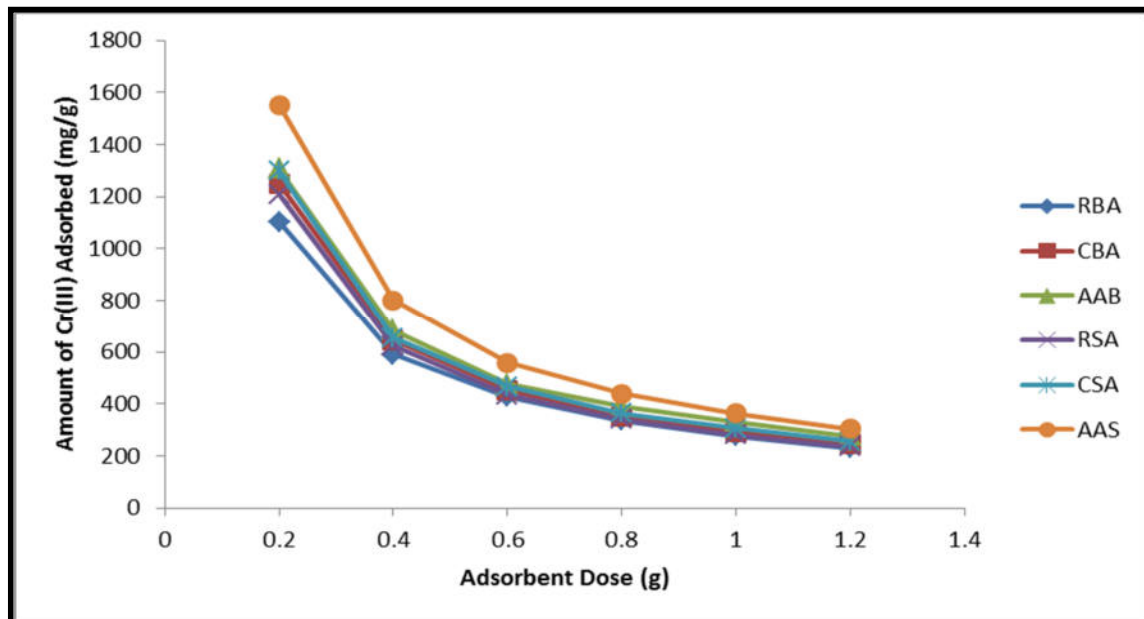


Figure 10: Influence of adsorbent dose on the amount of Cr³⁺ ions adsorbed.

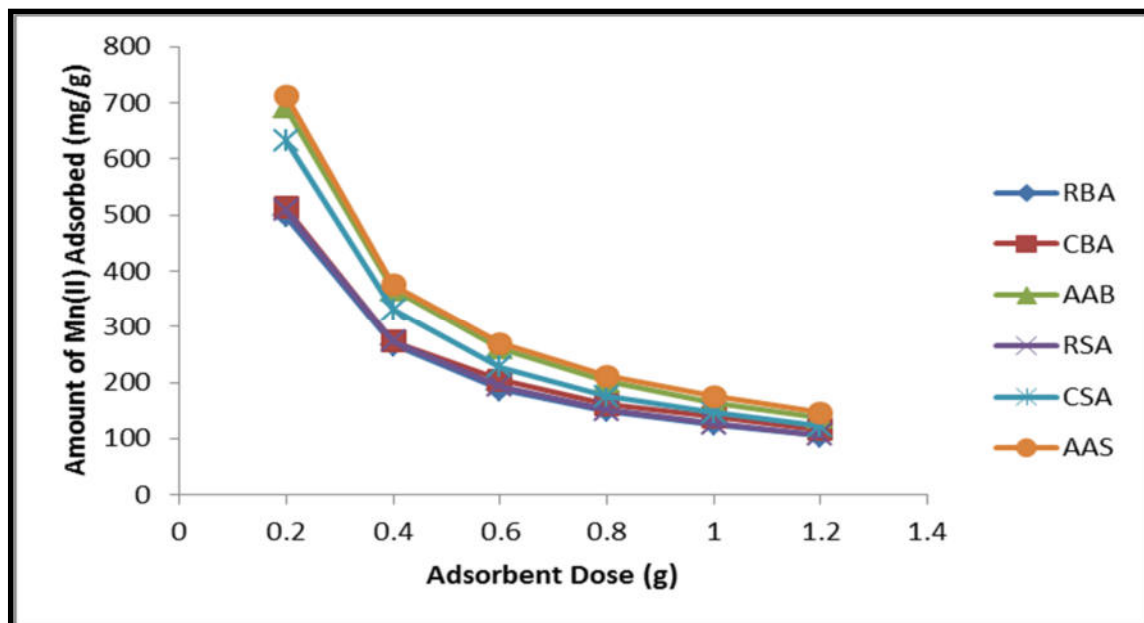


Figure 11: Influence of adsorbent dose on the amount of Mn²⁺ ions adsorbed.

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.

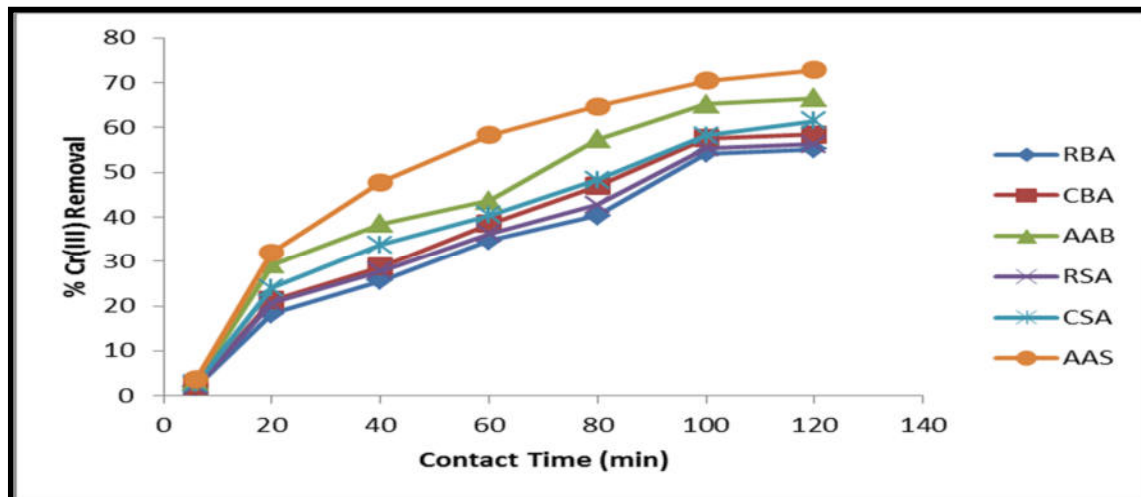


Figure 12: Time dependent study on the sorption of Cr^{3+} ions onto adsorbents prepared from shale and bentonite

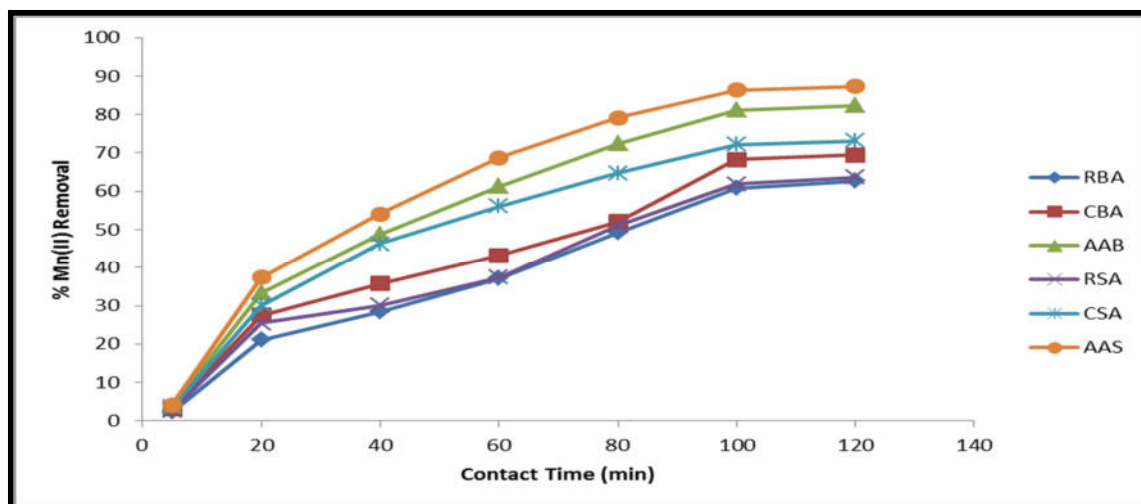


Figure 13: Time dependent study on the sorption of Mn^{2+} ions onto adsorbents prepared from shale and bentonite

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

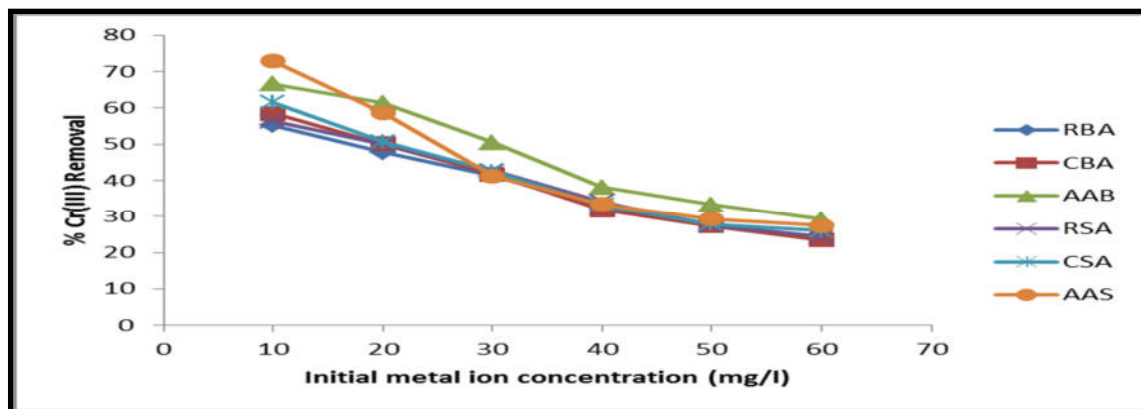


Figure 14: Effects of initial metal ion concentration on the adsorption efficiency of Cr^{3+} ions onto adsorbents prepared from shale and bentonite.

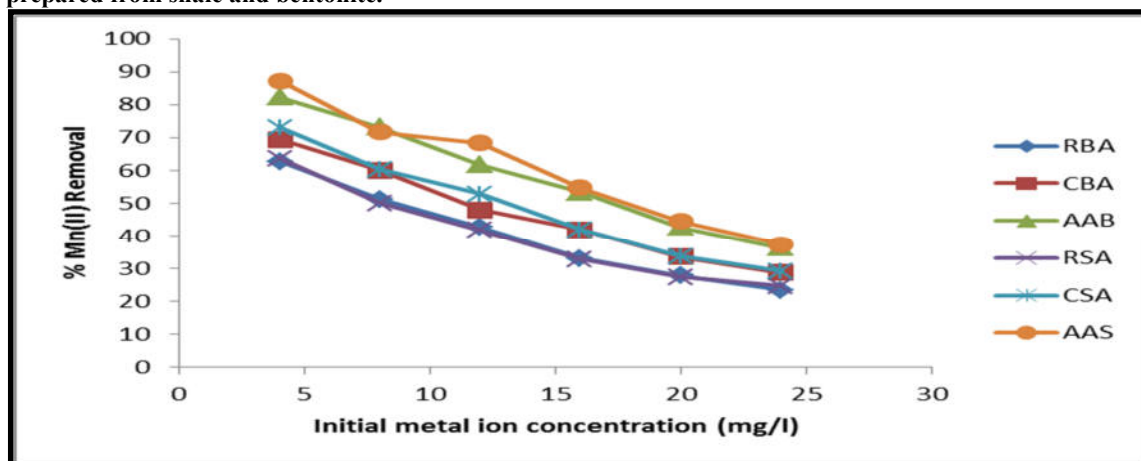


Figure 15: Effects of initial metal ion concentration on the adsorption efficiency of Mn^{2+} ions onto adsorbents prepared from shale and bentonite

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

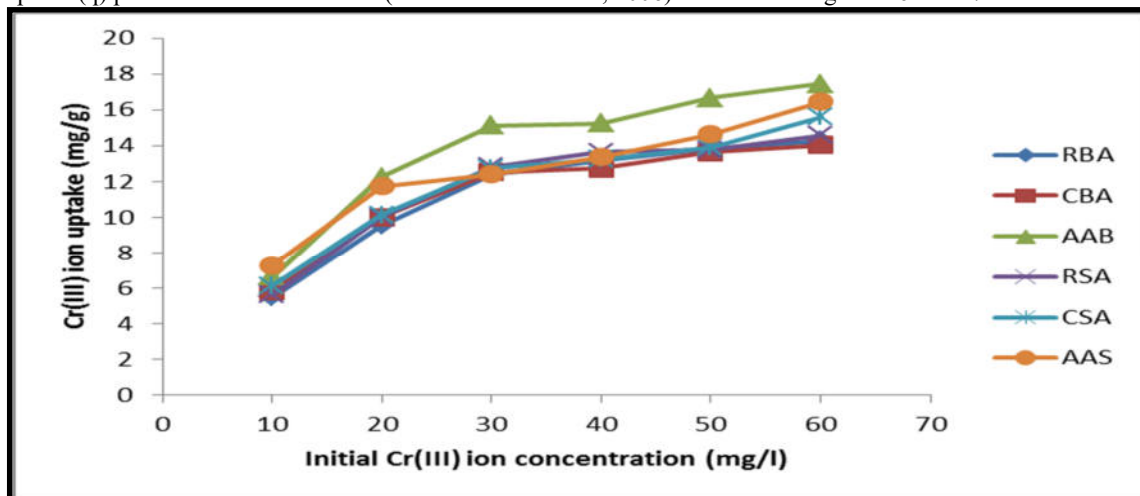


Figure 16: Effects of initial metal ion concentration on the uptake of Cr³⁺ ion by unit mass of adsorbents prepared from shale and bentonite

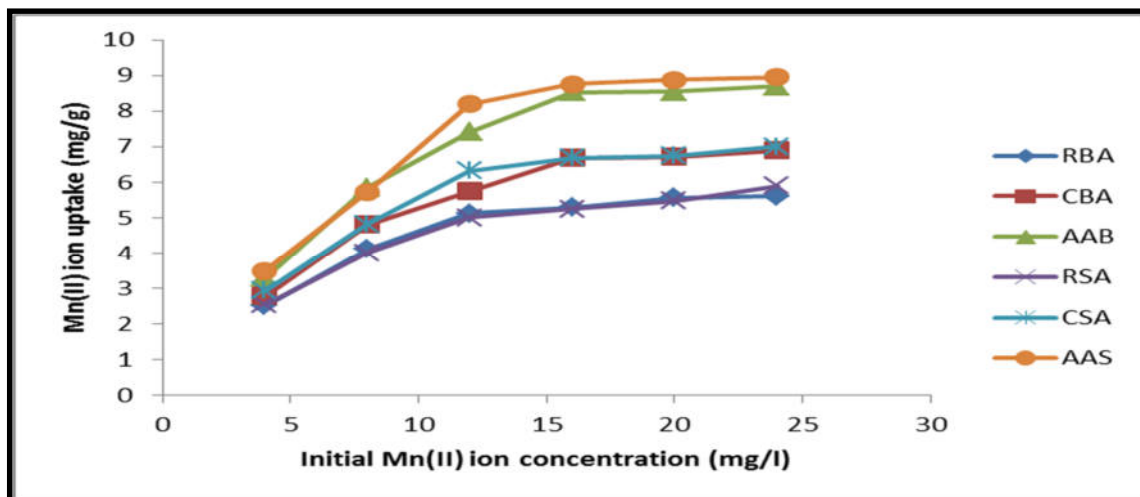


Figure 17: Effects of initial metal ion concentration on the uptake of Mn²⁺ ion by unit mass of adsorbents prepared from shale and bentonite

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

Table 2: Statistics of Cr³⁺ ion removal

Efficiency of Cr(III) ion Removal (%)								
	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
AAS	6	43.817	18.2024	7.4311	24.714	62.919	27.4	72.8
CSA	6	40.233	13.9308	5.6872	25.614	54.853	26.0	61.4
RSA	6	29.000	12.9533	5.2882	15.406	42.594	13.3	46.3
AAB	6	46.450	15.3740	6.2764	30.316	62.584	29.1	66.5
CBA	6	38.783	13.7016	5.5937	24.404	53.162	23.4	58.4
RBA	6	27.883	12.3989	5.0618	14.871	40.895	12.8	45.1
Total	36	37.694	15.2285	2.5381	32.542	42.847	12.8	72.8

Table 3: Statistics of Mn²⁺ ion removal

Efficiency of Mn(II) ion Removal (%)								
	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
AAS	6	60.617	18.6308	7.6060	41.065	80.168	37.3	87.3
CSA	6	48.467	16.7240	6.8275	30.916	66.017	29.2	73.1
RSA	6	30.033	14.8971	6.0817	14.400	45.667	14.6	53.6
AAB	6	58.233	17.6992	7.2257	39.659	76.808	36.2	82.3
CBA	6	46.917	15.5925	6.3656	30.553	63.280	28.7	69.4
RBA	6	30.167	14.9807	6.1159	14.445	45.888	13.4	52.7
Total	36	45.739	19.5670	3.2612	39.118	52.359	13.4	87.3

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 4: Equal variance assumption

Efficiency of Cr ³⁺ Removal	Test of Homogeneity of variance			
	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 Cr³⁺ and Mn²⁺ 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^{3+} and Mn^{2+} ion removal. To select the best adsorbent for the removal of Cr^{3+} and Mn^{2+} ion, the mean plot of performance against the selected adsorbent as presented in Figures 18 and 19 were employed.

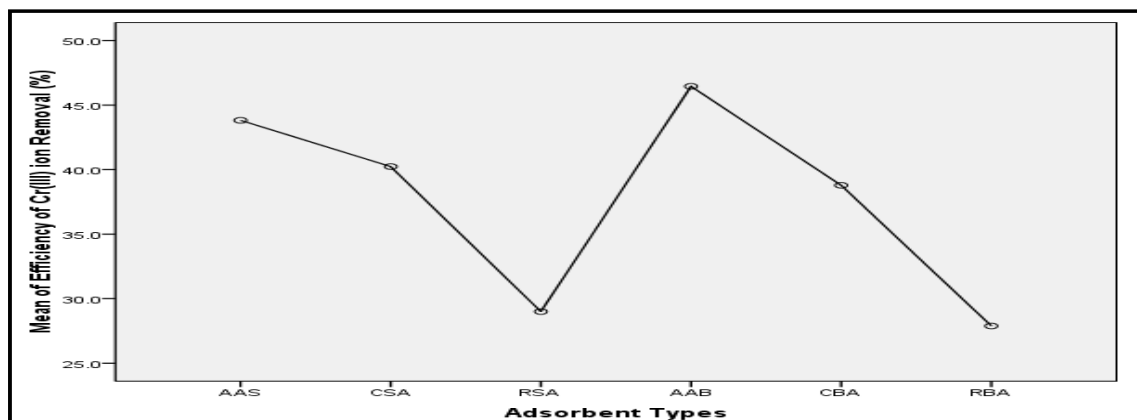


Figure 18: Best adsorbent for Cr^{3+} ion removal

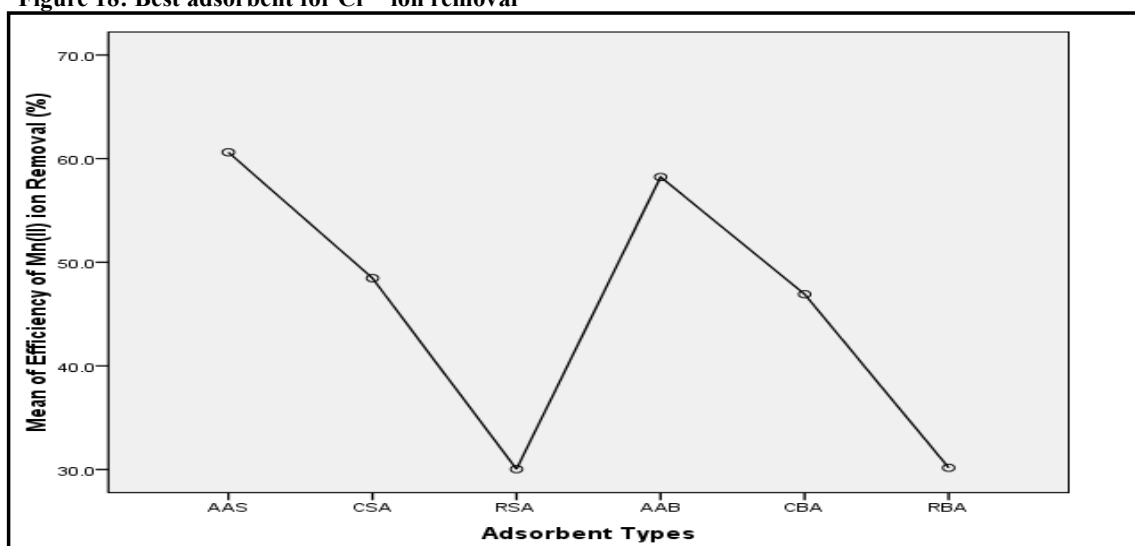


Figure 19: Best adsorbent for Mn^{2+} removal

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

5. References

1. Abd El-Latif M.M. and Amal I.H., (2009), Adsorption, kinetic and equilibrium studies on the removal of basic dye from aqueous solutions using hydrolyzed Oak Sawdust, Desalination and Water Treatment Publication, Vol. 6, 252-268.
2. Badmus, M.A.O.; Audu T.O.K and Anyata, B.U., (2007), Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells, Turkish Journal of Engineering and Environmental Science, 251 – 263

3. Dwayne, D (2010), Examining differences, comparing groups using SPSS; Inferential Statistics (part 1), 1-42
4. Garg, V.K; Gupta, R; Yadav, A and Kumar, K (2003), Dye removal from aqueous solution by adsorption on treated sawdust, *Bioresource Technology Journal* vol. 89, 121-124
5. Gimbert, F.; Morin-Crini, N.; Renault, F.; Badof, P.M and Crini, G., (2008), Adsorption isotherm models for dye removal by cationized starch-based materials in a single component system; Error analysis, *Journal of Hazardous Materials*, Vol. 157, 34-46
6. Gunay, A.; Arslankaya, E and Tosun, I., (2007), Lead removal from aqueous solution by natural and pretreated clinoptilolite; adsorption equilibrium and kinetics, *Journal of Hazardous Materials*, Vol. 146, 362-371
7. Hao, C and Wang, A., (2007), Kinetic and isothermal studies of lead ion adsorption onto polygorskite clay, *Journal of Colloid and Interface Science*, vol. 307, 309 – 316
8. Hong, Z.; Donghong, L.; Yan, Z.; Shuping, L., and Zhe, L., (2009), Sorption isotherm and kinetic modeling of aniline on Cr-bentonite, *Journal of Hazardous Materials*, vol. 167, 141 – 147
9. Ilaboya, I.R., (2017); Studies on the removal of some heavy metals by adsorption using shale, unpublished PhD thesis submitted to the Department of Civil Engineering, University of Benin, Benin City
10. Johnson, B.B (1990), Effect of pH, temperature and concentration on the adsorption of cadmium on goethite, *Environmental Science Technology Journal*, vol. 24, 112-118
11. Krishna, G.B and Susmita, S.G (2006), Adsorption of chromium (VI) from water by clays, *Industrial Engineering and Chemical Resource Journal*, vol. 45, 7232-7240
12. Lin, S. H., and Juang, R.S., (2002), Heavy metal removal from water by sorption using surfactant-modified montmorillonite, *Journal of Hazardous Materials*, vol. B92, 315 – 322
13. Low, K.S; Lee, C.K and Lee, K.P (1993), Sorption of copper by dye-treated oil palm fibers, *Bioresource Technology Journal*, vol. 44, 109-112
14. Mariadas, K.; Kalyani, G.; Joga, H.R.; Kumar, P. Y and King, P., (2012), The removal and equilibrium studies of cadmium by natural clay as adsorbent, *International Journal of Scientific Engineering Research*, Vol. 3(8), 1-6
15. McKay, G; Otterburn, M.S and Aja, J.A (1985), Fuller's earth and fired clay as adsorbent for dyes stuffs, *Water Air and Soil Pollution Journal*, vol. 24, 307-313
16. Omisanya, N.O.; Folayan, C.O.; Aku, S.Y and Adefila, S.S., (2012), Synthesis and characterization of zeolite for adsorption Refrigeration application, *Advance in Applied Science Research*, Vol. 3(6), 3746-3754
17. Omokaye, (1999), Final report on the post impact assessment study of the Jesse oil spill/fire incident site, an unpublished investigation report submitted to pipeline and product marketing company (PPMC)
18. Ong, S.; Seng, C., and Lim, P., (2007), Kinetics of adsorption of copper (II) and cadmium (II) from aqueous solution on rice husk and modified rice husk, *Electronic Journal of Environmental Agriculture and Food Chemistry*, Vol. 6(2), 1764-1774.
19. Qadeer, R., and Hanif, J., (1994), Kinetics of zirconium ions adsorption on activated charcoal from aqueous solution, *American journal of Biochemistry and Biotechnology*, Vol. 3 (2), 34 – 43
20. Saeed, A; Akhter, M.W and Iqbal, M (2005), Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, *Separation and Purification Technology Journal*, vol. 45, 25-31
21. Uzun, H; Bayhan, Y.K; Kaya, Y; Cakici, A and Algur, O.F (2003), Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus Sylvestris*, *Desalination Journal*, vol. 154, 233-239
22. Weng, C.H; Tsai, C.Z; Chu, S.H and Sharma, Y.C., (2007), Adsorption characteristics of copper (II) onto spent activated clay, *Separation Purification Technology Journal*, vol. 54, 187-197
23. Yu, L.J; Shukla, S.S; Dorris, K.L; Shukla, A and Margrave, J.L (2003), Adsorption of chromium from aqueous solution by maple sawdust, *Journal of Hazardous Materials*, B100, 53-59

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