Adsorption Treatment of Industrial Paint Effluent for the Removal of Pollutants by Local Clays

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Abstract: The use of local clay as an adsorbent for the removal of metal ions, such as, lead, chromium, silver, iron and copper from paint effluent, was investigated. In this work, adsorption of these metals onto the modified clays was studied through a process involving coagulation. Satisfactory results were obtained. Local clays have been considered a potential adsorbent for the removal of pollutants from industrial paint effluent. The effective application of local clays for effluent treatment is limited due to small surface area and presence of net negative surface charge leading to its low adsorption capacity. This work was focused towards modifying the physical structure and chemical properties of the clay to maximize its adsorption capacity. The problem of clean water can be solved by treating industrial and municipal waste water with modified clays. The treated effluents were analyzed for the concentration of chromium, potassium, lead, magnesium, manganese, iron, cobalt, sodium, silver, mercury and cadmium. Also some gross organic pollution indicators such as biological oxygen demand (BOD) and chemical oxygen demand (COD) as well as pH, acidity, alkalinity, turbidity, hardness and total dissolved solids (TDS) of the effluents were determined. The study showed a percentage removal of over 50% for all the contaminants. The modified clay was at its best performance when calcined at 650oC. The results of this study showed that the modified clays were appropriate for the treatment of industrial paint effluent.

Key words: Modified clay, paint effluent, calcination, acid treatment, BOD, COD

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1.0 Introduction

Paint effluents contain high amounts of heavy metals and organic pollutants therefore, the removal of these toxic pollutants from effluent before discharging to the environment and from raw water before public use is essential for the protection of health and environment.

The groundwater in industrial areas across the country has undergone severe contamination by industrial waste, effluents and emissions which are discharged indiscriminately without any regulatory system. However in the wake of recent industrialization and fast urbanization the quality of groundwater has become an increasing concern due to contamination by various toxic chemicals (Abskharan et al, 2009). The net effect is heavy metal poisoning, and concentration in the water making water unfit for consumption and difficult for reuse. In order to make water usable after water pollution, it must be treated with a variety of filtration and purification methods. (Sharma and Agrawal, 2005).

Industrial effluents not only contain nutrients that enhance the growth of crop plants but also have other toxic materials. The impact of toxicity was evident as visible symptoms of chlorosis, yellowing and immature fall of leaves, poor growth and retarded flower, fruit and green yields.

Wastewater from textile industry has the highest amount of heavy metals rendering them most hazardous for soil, plant and other organisms including human being. These industrial effluents with heavy metals could be toxic and accumulated in the receiving environment, causing adverse effects on indigenous biota.

Several methods have been adopted for the removal of these pollutants from industrial effluents, which includes: chemical precipitations, conventional coagulation, reverse osmosis, ion-exchange, solvent extraction, membrane filtration, chemical precipitation, electrodialysis and lime coagulation, oxidation and reduction method. However, the selection of wastewater treatment method is based on the concentration of the pollutants in the effluent, the efficiency and cost of the process operation relative to other techniques. These techniques are not only expensive but also inefficient in complete removal, high reagent and energy requirements and generation of toxic sludge. However, they require high level of expertise to operate and maintain the process.

Adsorption has been found to be the most efficient method for the removal of pollutants from effluents (Al-Khatib et al, 2012). The effectiveness of an adsorbent depends on the adsorptive properties of their surface. The sorption of these pollutants from aqueous solutions is an important process in wastewater treatment. The use of adsorbents such as clay has also been found to circumvent the production of large amounts of sludge usually generated using alternative wastewater treatment techniques. Clays have a tremendous number of miscellaneous uses, and for each application a distinct type with particular properties is important. Recently, clays have become important for various aspects of environmental science and remediation (Chukwujike et al, 2015). Clays are therefore considered alternative adsorbents which can compare favorably not only in terms of cost effectiveness, but also efficiency, and readily available in abundance. However, modifications of the clay minerals using different methods such as acid, alkali and thermal treatment increases greatly the adsorption potentials of clays for pollutants removal from effluents.

In general, natural clays possess electrically charged and hydrophilic surface characteristics due to isomorphous substitutions in their crystal lattice and thus they are very efficient adsorbents of heavy metals and polar molecules. The application of clay for the removal of non-ionic organic pollutants, on the contrary is limited. Acid activation is one of the most common chemical methods of clay treatments. This process results to increased specific surface area, porosity and

surface acidity (Komadel, 2003). Important parameters for the acidification, which determines the properties of the products, include the nature and type of clay, acid concentration, temperature and activation time. In addition, this acid activation is believed to promote catalytic activity of the clay by increasing the number of Bronsted and potential lewis sites.

2.0 Materials and method

2.1. Materials

The clay used in this study was sourced locally from Nsu Imo State, Nigeria. The paint effluent used was collected from Home Pride Paint Industries, Km 12 Onitsha-Enugu Express Way, Ogbunike, Oyi LGA, Anambra State. The following analytical grade chemicals such as Hydrochloric acid, ammonium, solochrome black tea, ethylene di-amine tetra-acetic acid, magnesium sulphate, alkali-iodide acid, phenolphthalein, potassium dichromate, mercuric sulphate solution were used without further purification.

2.2. Preparation of clay sample

The local Nsu clay was hand dug, crushed to coarse particles, sun-dried, to remove dirt and particles and calcined at high temperature ($650^{o}C$) for three hours. The calcined clay samples were taken into a clean dry mortar and crushed into fine particles. The fine particles were then sieved through a mesh size of 0.075mm and stored in dry air-tight containers for subsequent studies. The small tiny particle size was chosen so as to improve adsorption. The particle size is an important factor in adsorption kinetics because it determines the time required for transport within the pores to adsorption sites.

2.3. Acid-Thermal activation

The acid-thermal activation was carried out in a rotary shaker with temperature and agitation control. The calcined clay samples were treated with HCl solution of known concentrations of 2M and 4M at room temperature. The acid to clay ratio was 1:1. Agitation was carried out using a rotary shaker at 1000rpm. The reaction was carried out for 3 hours after which the reaction was terminated with the addition of large quantities of distilled water. The samples were exhaustively washed until free of ions and a pH of 6 was maintained. The acid activated samples were centrifuged and dried in an oven for 1 hour. The samples were then subjected to thermal activation at $100^{o}C$ for 20 minutes. The solid mass was then cooled in a desiccator and pulverized and stored in air-tight plastic containers for further use.

2.4. Characterization of clay samples

The surface area of the clay sample was estimated using Sear's method as described by (Al-Qadah and Shawabkah, 2009). Heavy metals analysis was determined using Varian AA240 Atomic Absorption Spectrophotometer (AAS) according to the method of APHA 1995 (American Public Health Association). The total solids, which includes the total suspended solids, and total dissolved solids were determined as described by (APHA; 1998).

2.5 Preparation of Effluent Sample

The paint effluent sample was thoroughly mixed by shaking, and 100ml of it was transferred into a glass beaker of 250ml volume, to which 5ml of concentrated nitric acid was added and heated to boil until the volume was reduced to about 15-20ml, by adding concentrated nitric acid in increments of 5ml until all the residues were completely dissolved. The mixture was cooled, and made up to 100ml using metal free distilled water. The sample was aspirated into the oxidizing air-acetylene flame. When the aqueous sample has aspirated, the sensitivity for 1% absorption was observed.

2.6 Preparation of Reference Solution

A series of standard metal solutions in the optimum concentration range was prepared, the reference solutions were prepared daily by diluting the single stock element solutions with water containing 1.5ml concentrated nitric acid/litre. A calibration blank was prepared using all the reagents except for the metal stock solutions. Calibration curve for each metal was prepared by plotting the absorbance of standards versus their concentrations.

3.0 Result and Discussion

3.1 Chemical Analysis of local clay

The chemical composition of the local clay have been studied, Table 1. The results revealed that silica and alumina form the major component of the clay (kaolin) while other oxides were present in minute amount as impurities. The result of the chemical composition of the raw clay was very close to that reported by Dawodu and Akpomie (2014), where they obtained silica to alumina composition of 53.9 and 27.9%, respectively. Thermal treatment of the clay resulted to an increase in the composition of alumina and silica from 57.52 to 62.0% and 25.29 to 28.02% respectively. The percentage increase was as a result of the pores which were opened thereby exposing the hidden elements during calcinations at 650°C. There was an observed decrease in the loss on ignition from 14.03 to 6.787% due to the removal of most of the volatile components of the clay during calcination. Acid treatment of the kaolinite with 2M HCl led to a decrease in

the alumina ratio from 25.29 to 18.83% and further decrease to 15.40% with increased acid concentration of 4M HCl.

Table 1: Chemical Composition of the Raw and Modified Clay.

Composition (%)	Raw Clay	Modified Clay		
		Calcined Clay (650^0C)	2M - HCl Clay	4M - HCl Clay
SiO_2	57.52	62.00	65.27	63.87
$AI2O3$	25.29	28.02	18.83	15.40
Fe_2O_3	0.11	0.11	0.21	0.21
TiO_2	0.85	1.93	0.53	0.65
CaO	0.251	0.188	0.33	0.28
MgO	-	-	-	-
Na_2O	0.30	0.17	0.45	0.32
K_2O	0.492	0.411	0.33	0.34
SO_3	-	0.130	-	-
MnO	0.0023	0.010	0.018	0.027
Se_2O_3	0.003	0.003	-	0.002
V_2O_5	0.23	0.130	0.29	0.22
Cr^2O^3	0.079	0.078	0.15	0.10
NiO	-	-	-	-
CuO	0.019	0.016	0.285	0.197
ZnO	-	-	0.09	0.11
BaO	-	0.15	-	-
L.O.I	14.03	6.787	13.217	18.27

3.2 Characterization of Local Clay

The specific surface area of a material is a very important property in determining the adsorption capacity of the material. Also, a high specific surface area (SA) is desirable for effective adsorption. In general it is expected that the higher the SA of a material the higher the adsorption potential, although not in all cases. The SA obtained for the clay investigated was found to be $32.1 m^2/g$. Kaolin with SA of 3m/g have been reported (Bhattacharyya and Gupta, 2006), and $19.8 m^2/g$ (Dawodu and Akpomie, 2014). The higher SA of the clay implies that the material would be effective in treatment of the contaminated effluent. The moisture content of the clay obtained was found to be 3%, an indication that most of the moisture (water) was evaporated

during calcination. This low moisture content was desirable because more pores were made available for the removal of contaminants from the effluent during the sorption process which involves the diffusion of water into and on the surface of the clay. The specific gravity investigated was 2.08g/ml comparative to the literature value of kaolin which ranges from 2.16 – 2.68g/ml. The bulk density of kaolin in the dried natural state reflects their mode of genesis. Those which originated as superficial weathered deposits or as deposits of either sedimentary kaolin or water-land materials which eventually formed kaolin, possesses relatively low bulk densities below 2.0g/ml. The bulk densities of kaolinites play important roles in its economic value when fired as refractory or adsorbent.

Table 2: Characterization of local clay

Parameter	Values
Surface area (m^2/g)	32.1
Moisture content (%)	3.0
Specific gravity	2.08
Bulk density (g/ml)	1.94

Table 3: Physicochemical Characterization of the Untreated Paint Effluent.

Parameters	Values	WHO Standard
pH	6.94	6.5-8.5
Turbidity NTU	928	5.0
Colour	Milkish white	-
Odour	Objective	-
Resistivity	3.0303	-
Alkalinity (mg/L)	165	100
Hardness (mg/L)	700	100
Calcium Hardness (mg/L)	174	-
Acidity (mg/L)	185.6	100
Conductivity $\mu s/cm^3$	0.33	100
Total Dissolved solid (mg/L)	70.9	50
Total Solid (mg/L)	15	50
Total Suspended solid (mg/L)	69.1	30
Sulphate (mg/L)	304.51	200
Phosphorous (mg/L)	6.7464	-

Nitrate (mg/L)	7.5438	50
Chloride (mg/L)	600	200
BOD (mg/L)	10.8	15
COD (mg/L)	433	40
Arsenic (mg/L)	3.510	0.01
Selenium (mg/L)	0.00	-
Aluminium (mg/L)	0.546	0.2
Calcium (mg/L)	61.184	75
Chromium (mg/L)	1.08	0.05
Cobalt (mg/L)	1.02	-
Manganese (mg/L)	0.948	0.1
Nickel (mg/L)	0.384	0.05
Copper (mg/L)	2.49	1.0
Silver (mg/L)	6.543	-
Cadmium (mg/L)	0.00	0.005
Sodium (mg/L)	51.332	200
Potassium (mg/L)	1.166	10
Lead (mg/L)	0.149	0.04
Magnesium (mg/L)	19.657	30
Iron (mg/L)	10.42	0.3
Mercury (mg/L)	0.00	0.001
Zinc (mg/L)	0.1497	5.0

3.3: Physicochemical analysis of the paint effluent.

The untreated effluents shown in table 3 depict highly polluted effluents. For instance the COD value was 433mg/L as against the maximum limit for COD which is 40mg/L as stipulated by WHO, 2003. This shows that the inorganic matter which was contained in the untreated effluent was highly toxic. Other parameters such as alkalinity, hardness, acidity, with heavy metals such as iron silver and copper were above the limit for effluent discharge, and this poses threat to lives. The results of the experiment carried out to assess the percentage removal of the pollutants from paint effluents at different levels of adsorbents are presented in table 4 and figures 1 to 8 respectively.

3.4 Treatment of the Paint Effluent

Due to the high concentration of some of the parameters obtained from the paint effluents which were higher than the WHO limits, the effluent was treated with the local and modified clay to reduce the concentrations of these parameters to acceptable limits. The raw clay (Raw-C), thermally activated clay (Calcined-C), and the 2M and 4M HCl treated calcined clay (2M-HCL-C and 4M-HCL-C) were utilized for the effluent treatment. The treatment of paint effluent using modified clay is shown in Table 4.

Table 4: Physiochemical analysis of the treated paint effluent

Parameters	Raw Clay	Calcined Clay	2M HCl-C	4M HCl-C
pH	3.60	3.90	4.54	4.00
Oxygen Demand 1	13.5	15.8	10.5	10.5
Oxygen Demand 2	6.6	7.8	5.9	5.9
Turbidity NTU	88.9	035	27.9	55.0
Total Dissolved Solid mg/l	5.3	0.8	0.04	1.6
Chromium ppm	0.00	0.00	0.00	0.00
Sodium ppm	48.904	10.085	34.923	44.589
Potassium ppm	0.993	0.691	0.28	0.43
Magnesium ppm	28.495	21.762	21.361	22.183
Lead ppm	0.00	0.00	0.00	0.545
Cobalt ppm	0.119	0.118	0.0126	0.240
Maganese ppm	0.027	0.228	0.987	0.936

Fig 1 gives a graphical representation of the total alkalinity of the paint effluent. The result showed a significant decrease in total alkalinity after treatment with the modified clays to acceptable levels which conforms to the WHO standard. The raw, calcined and acid treated clays were found to decrease drastically the concentration of the total alkalinity when compared to the initial concentration in the paint effluent. The treatment with 4MHCl –C recorded the highest decrease in alkanity.
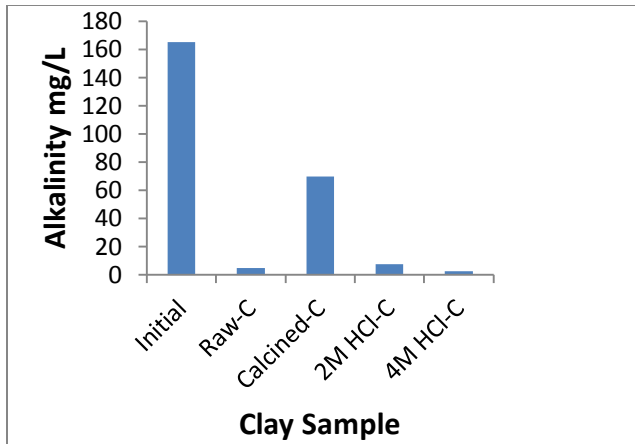
 Fig 1: Total Alkalinity of the Paint Effluent before and after Clay Treatment.

The total hardness of the paint effluent after treatments with modified clays was found to decrease at all the treatments studied with the calcined clay recording the highest decrease of 260mg/L, see Fig 2. Similarly all the clays recorded a decrease in the total hardness of the effluent after treatment.
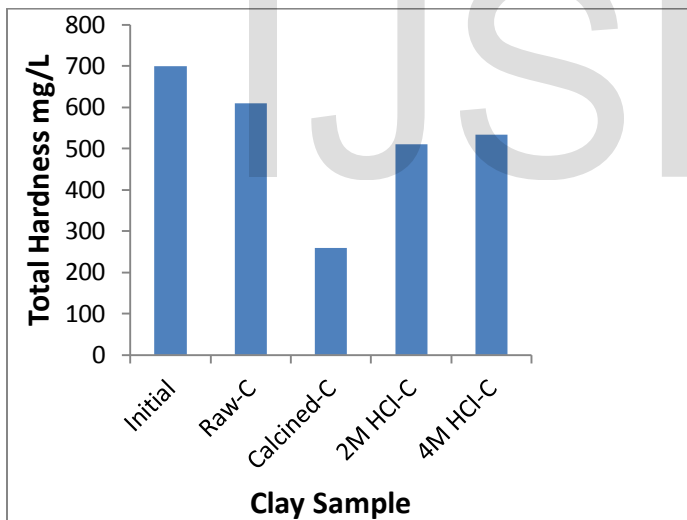

Fig 2: Total Hardness of the Paint Effluent before and after Clay Treatment.

Treatment with the 4M-HCl resulted to a high increase in the total acidity of the effluents from 185.6 to 267.5mg/L possibly influenced by the acidic nature of the clay. This high acidity of the clay can be reduced by treatment with calcium oxide. All the clay treatments showed percentage increase in acidity.
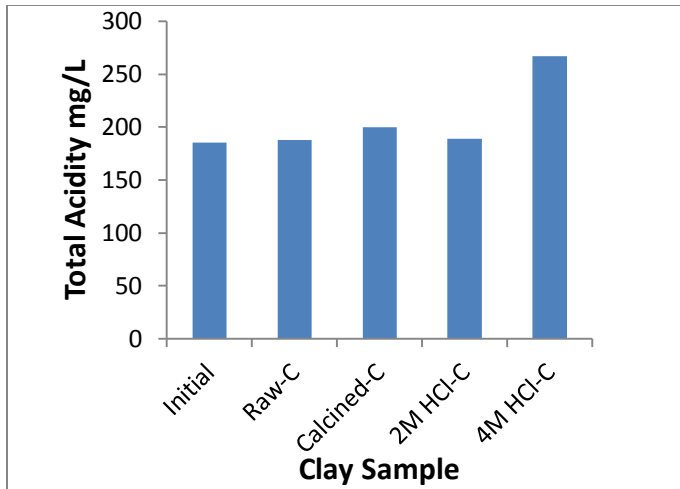
 Fig 3: Total Acidity of the Paint Effluent before and after Clay Treatment.

More importantly, the chemical oxygen demand (COD) of the effluent decreased significantly for all clay treatments used .The raw and calcined clays recorded the highest decrease in the COD of the effluents. A decrease in the BOD of the effluent was also obtained for various clay treatments, with the best performance obtained for 2M HCl-C.
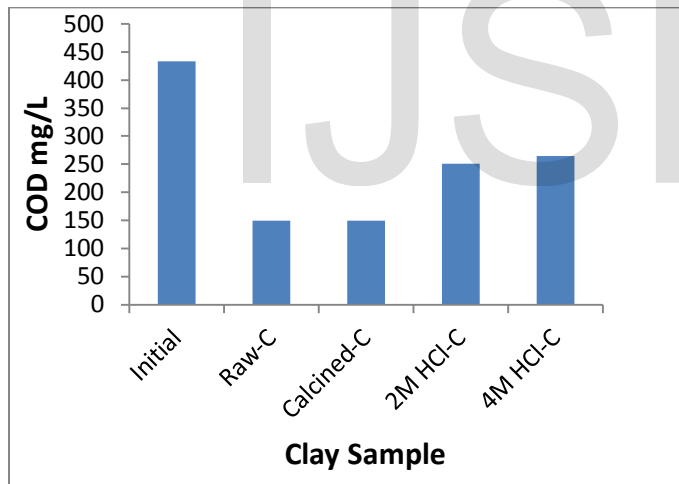

Fig 4: Chemical Oxygen Demand (COD) of the Paint Effluent before and after Clay Treatment.
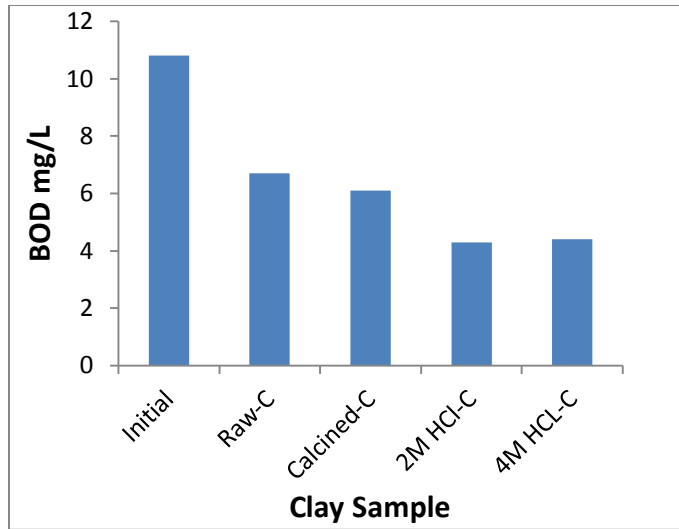
Fig 5: Biochemical Oxygen Demand (BOD) of the Paint Effluent before and after Clay Treatment.

A general decrease in the concentration of all the metals was recorded for all the clay forms in the treated effluent. Similarly, decrease in heavy metal concentration from contaminated solutions after clay treatments have been reported (Unuabonah et al, 2008). The 2M HCl-C was found to be more effective for the reduction of potassium magnesium and cobalt. However, the calcined clay was generally found to be at its best performance in the effluent treatment.

A great reduction in the iron concentration of the effluent was obtained for all the clay forms used in the treatment, Fig 6. The treatment with calcined and 2M HCl clay were found to be the best adsorbent for the removal of iron for the effluent with a high reduction from 10.42mg/L to 1.967 and 3.025mg/L, respectively.
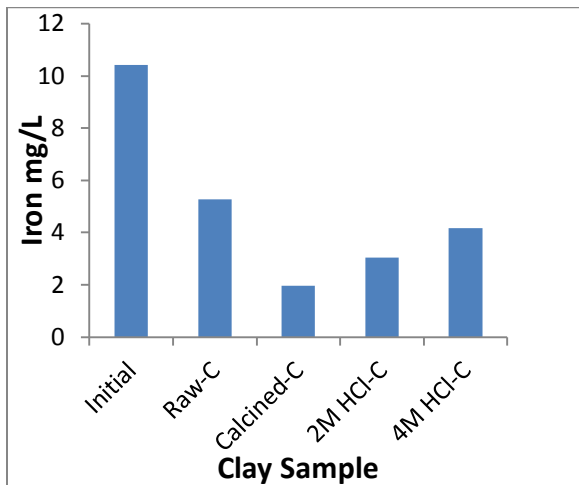

Fig 6: Iron Concentration of the Paint effluent before and after Clay Treatment.

It was observed that a high reduction in the silver content of the effluent was obtained for all the clay adsorbents used. This indicates that the clay investigated was an excellent adsorbent for silver ions seen from the effective reduction in the concentration of silver in the effluent from 6.543 to 0.183 shown by raw clay, and the modified clay showed its best performance.
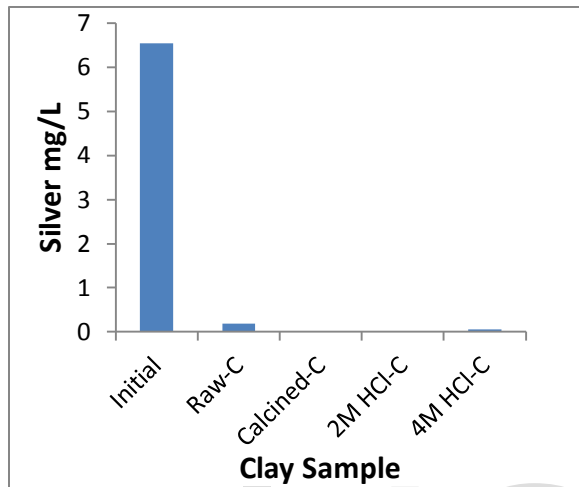

 Fig 7: Silver Concentration of the Paint Effluent before and after Clay Treatment.

This study showed a great reduction in the copper concentration of the effluent after treatments for all the clay forms used with the 4MHCl-C at its best performance.
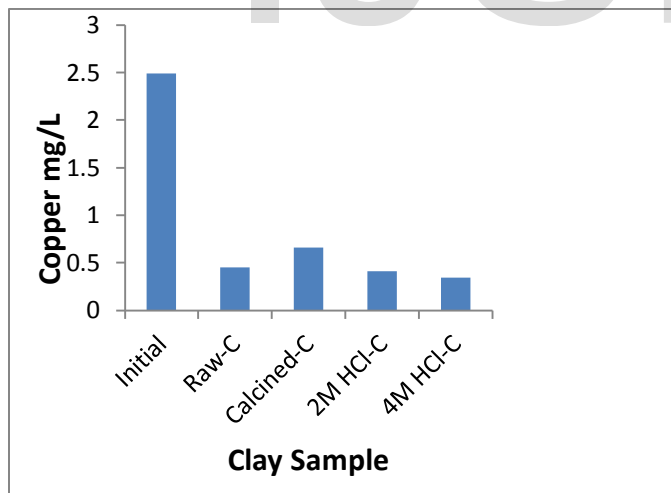

Fig 8: Copper Concentration of the Paint Effluent before and after Clay Treatment.

4.1 Conclusion

The applicability of clay minerals and its modified forms in the removal of pollutants from paint effluents has been studied. The use of modified clays has proven to be very viable for paint effluent treatments. Modified clays operate via partitioning phenomena and have a synergistic

effect with activated carbon and other unit processes such as reverse osmosis. They have proven to be superior to any other water treatment technology in applications where the water to be treated contains substantial amounts of oil and grease or humic acid, and toxic organs. The commercial application of modified clays to trihalomethane control in drinking water has not yet occurred. With increasing concerns about the carcinogenic effects of trihalomethanes, the commercialization of this technology could be around the corner.

This study has highlighted the thermal-acid treated clay, best adsorbent due to the removal of water of hydration and increase in the surface area of the clay when calcined at high temperature (650°C). Data from this study proved that metal cations from paint effluent can be adsorbed successfully in significant amounts by modified Nsu clay. This opens up new possibilities and potential commercial uses in the clay market

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