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Modification and Physiochemical Characterization of Kaolin Clay for Adsorption of Pollutants from Industrial Paint Effluent

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ABSTRACT

The design of wastewater treatment methods is usually based on the need to reduce heavy metals and suspended solid loads to limit pollution of the environment. The quality of treated effluent used in agriculture has a great influence on the operation and performance of the wastewater-soil-plant or aquaculture system. In the case of irrigation, the required quality of effluent is dependent on the crops to be irrigated, the soil conditions and the system of effluent distribution adopted. The present study is aimed to provide a healthy and better environment for both man and aquatic bodies. In this study, Nsu clay was modified by thermal and alkaline process for the removal of heavy metals and organic pollutants from industrial paint effluent. The modified clay was used to purify effluent from paint industry through a process involving coagulation for colour and sorption. The treated effluents were analyzed for the heavy metal concentration such as chromium, potassium, lead, magnesium, manganese, iron, cobalt, sodium, silver, mercury and cadmium. Furthermore, 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 studied. It was found that percentage removal was over 60% for all the contaminants. The modified clay exhibited better performance when calcined at 750^{o}C with 4M NaOH. Application of the simple and low cost modification technique employed in this study makes kaolinite a co-effective adsorbent for removal of many organic and inorganic pollutants from industrial paint effluents.

Key words: Kaolin clay, paint effluent, adsorption, pollutant, thermal treatment, coagulation

INTRODUCTION

There have been increased concerns on the level of pollution caused by waste water which contained heavy metal ions, dyes and organic substance on the environment due to their toxic nature to man, plants, animals and aquatic life. These pollutants usually get into the environment from industrial effluents as a result of rapid industrial growth in most developing nations [1]. The disposal of industrial effluents has always been a major environmental issue. Pollutants in industrial effluents are always very toxic that the effluent has to be treated before its reuse or disposal in water bodies. These heavy metals are usually non-biodegradable, persistent in nature and very toxic even at certain low concentrations [2], causing serious health hazards such as cancer, headache, liver and kidney damages when present above the threshold limit in humans. Dyes are used for coloring purposes in textile, food, paper, carpet, rubber, cosmetic and plastic industries. Over 735 tons of synthetic dyes are produced annually worldwide and during the coloring processes approximately 10–15% of them are lost to waste streams as pollutants. Some of these dyes are toxic and suspected to have carcinogenic and mutagenic effects, some present an aesthetic problem and affect the nature of water reducing photosynthetic activity by inhibiting sunlight penetration [3]. Similarly persistent organic pollutants have been known to be very detrimental to humans and animals.

Paint production is one of the viable Small and Medium Scale Enterprises (SMEs) in Nigeria. Effluents from paint industries are among the problematic environmental issues faced by the Nigerian Chemical Manufacturing Sector. Paint effluents have been reported to contain a high amount of heavy metals and organic pollutants [4] Paint making itself involves the mixing of different chemical compounds which could result in excessive discharge of some organic and inorganic substances to the environment [5]. Since most of the heavy metals contained in paint effluents are non-biodegradable into toxic end products, their concentrations must be reduced to acceptable levels before discharge into the environment. Otherwise, these could pose a serious threat to public health and could affect the aesthetic quality of portable water.

Several methods have been adopted over the years for the removal of these pollutants from industrial effluents, which includes: chemical precipitations, conventional coagulation, reverse osmosis, ion-exchange, solvent extraction, membrane filtration, oxidation and reduction method and adsorption. 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. Adsorption is one of the most popular techniques and has been found to be the most efficient method for the removal of pollutants from effluents [6]. Since the mass of the water to be purified is generally large, the adsorbent to be used in the process should possess high selectivity with respect to the pollutants, be non-toxic, easily recoverable from filters, relatively cheap and readily available [7]. The sorption of these pollutants from aqueous solutions is an important process in wastewater treatment. The use of adsorbents has also been found to circumvent the production of large amounts of sludge usually generated using alternative wastewater treatment techniques [8]. Commercial activated carbon and zeolites (ion-exchange resin) have over the years been found to be the most effective adsorbent for pollutants removal from industrial effluents [9]. However, they are not only expensive but also not readily available, especially in third world countries like Nigeria. This has led to the search for alternate materials which could be used favorably because of their efficiency, cost effectiveness and natural resource availability. Consequently, several low cost and effective adsorbents have been utilized by many researchers which include biomass materials, sawdust, microorganism, sand soil, lateritic materials, red mud, charcoal and clay [10-13].

Different clay minerals such as montmorillonite, kaolinite and bentonite recorded good adsorption potential for pollutants removal from effluents, but with less effectiveness when compared to activated carbon [13, 14]. However, modification of the clay minerals using different methods such as acid, alkali and thermal treatment have been reported to increase greatly the adsorption potential of clays for pollutants removal from effluents [9]. Some are more effective towards cations (montmorillonite) and others are more effective towards anions (Kaolinite). There are two different mechanisms used in clay adsorption namely the cation exchange in the interlayer resulting from the interactions between ions and negative permanent charge and through the formation of inners sphere complexes through Si-O- and Al-O- groups at the clay particle edges [15]. Nigeria is blessed with abundance of clay minerals which are easily accessible, eco-friendly and can be utilized as low cost adsorbents for the removal of pollutants from industrial effluents. One of such is Nsu clay which is available in abundant found in Imo state Nigeria.

Until recently, very little knowledge was known about the fundamental nature of most clay materials. With the development of X-ray diffraction analysis, it was found that soil materials are composed of crystalline particles and that a limited number of different crystalline minerals are likely to be found in them. Clay minerals consists of hydrated aluminum silicates, whose crystalline structure is based on a combination of coordinated polyhedrons (tetrahedrons and octahedrons), arranged along planes [16]. In each tetrahedron (T), a silicon atom is equidistant from 4 oxygen atoms. These form in a regular pattern making up a tetrahedron. The chemical relationship of each tetrahedron may be expressed as SiO_4. These tetrahedrons of silica are linked together to form a hexagonal network of the composition Si-O when repeated indefinitely (Figure 1). The tops of the four tetrahedrons all point in one direction and the bases are all in one plane.

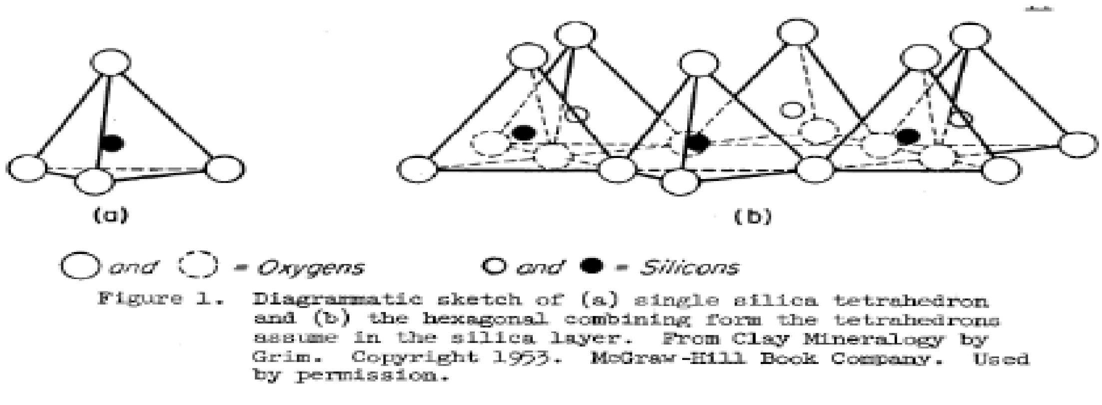


Fig. 1 (a) Single silica tetrahedron and (b) the hexagonal which combine to give the tetrahedrons in the silica layer.

Octahedrons (O) are generally coordinated by Aluminum and (or) Magnesium atoms, with oxygen atoms and -OH groups at the six vertices of the octahedron at the silica layer. The second layer or structural unit involved in the atomic lattices of most of the clay minerals is the alumina or Aluminum hydroxide unit. This layer consists of two sheets of closely packed oxygen or hydroxyls between which Aluminum atoms are embedded in such a position that they are equidistant from 6 oxygens or hydroxyls.

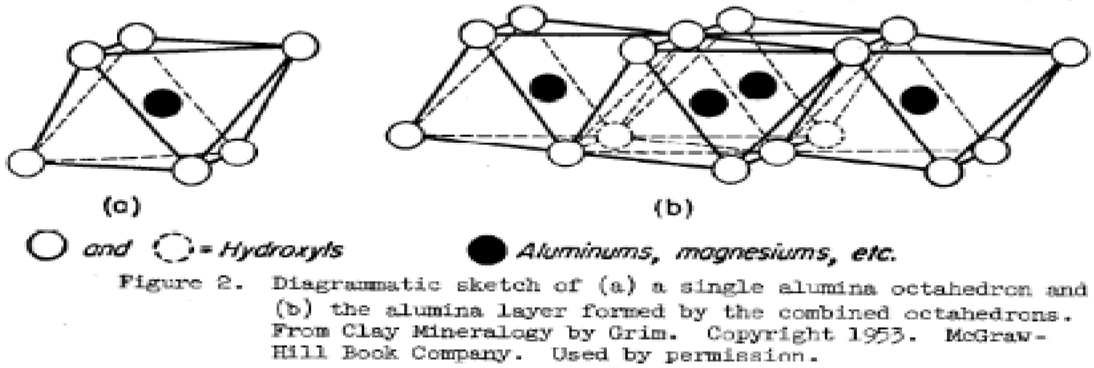


Fig 2. (a) a single Alumina octahedron and (b) the Alumina layer formed by the combined octahedrons. In the Alumina layer, only two-thirds of the possible central positions are filled with Al atoms. This is called gibbsite structure, and it has the formula $Al_2(OH)_6$. When magnesium is substituted for aluminum, all positions were filled to balance the structure which is brucite structure, $Mg_3(OH)_6$ [17].

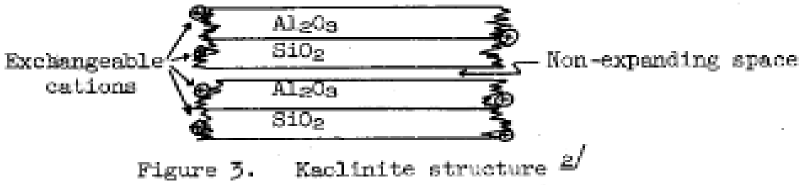


Fig. 3 Kaolinite structure

Calcination is another well-known treatment for the activation of clay adsorbents. Heating can bring about the modification of structure, physiochemical properties and composition of the clay minerals, including strength, cohesion, consistency limits, water content, maximum dry density, internal friction angle, particle size, permeability and specific gravity [18]. Additionally, the thermal treatment can assist stabilization of the clay to maintain important permanent properties. These concomitant changes can be varied from one clay mineral group to the other, as well as the particle size and heating regime. Raising the temperature to dehydration stage leads to a loss of adsorbed water causing alteration of the macro and micro-porosity of the clay minerals, resulting in the collapse of interlayer spaces and reduction of cation exchange capacity (CEC). Partial loss of the adsorbed and hydration water can increase hydrophilicity and surface acidity of the materials [19]. The heat treatment can also be preceded by other surface treatments such as chemical modifications, to achieve better performance. Heller-kallai [18] reported that thermal treatment of clay material can be carried out in different forms without any pretreatment mixed with various reagents before heating, after pretreatment and after pre-heating and pretreatment and subsequent re-heating. The degree of thermal tolerance can vary depending upon the clay types. Dehydration at a high temperature can cause the irreversible collapse of the structure [19]. The clay platelets are bonded electrostatistically. Therefore, dehydration of cation can result in a reduced adsorption ability of the clay [20]. Malo et al [21] studied the effect of heating kaolinite and bentonite and reported gradual increase in the strength of the clays and clay sediments with an increase in heating temperature. Such significant and permanent increase in their strengths occurred only after dehydroxylation at high temperature. By continuing heating to a temperature above the dehydroxylation stage, the clays became resistant to disintegration upon immersion in water [21]. Thus, thermo-analytical measurement of the clay minerals is often performed to understand the stability of their structure against an elevated temperature gradient. The effects of thermal and chemical treatments on physical properties of kaolinite was reported [22]. Modification of the clay structure after heat treatment at 500 ^oC for 5hrs was evidenced by the changes of the XRD pattern, where there was the formation of an amorphous phase in the thermally treated clay. This was related to the loss of hydroxyl groups, which cause a rearrangement of the original structure of kaolinite. Rytwo and Gonen [23] studied the morphological changes of the calcined bentonite and its adsorption efficiency towards nickel in the porous bed. The clay was treated at 500 ^oC for 24 hrs to increase its mechanical resistance and to eliminate some impurities. Report showed that calcinations lead to an increase in the clay surface area and the development of micro and mesoporosity due to bonded water release and de-hydroxylation. This resulted to a reduction in clay density compared to the untreated one, while the adsorption of nickel in clay pores resulted in slight increase in actual density. 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 [24]. The application of clay for removal of non-ionic organic pollutants, on the contrary is limited. Surface modifications using functional polymers is one of the methods applied to clay minerals in order to improve their adsorption capacities for non-ionic organic substances. This surface modifications of the clay minerals are generally carried out by two main approaches. Physical adsorption and chemical grafting of functional polymers to the surface of the clays [25]. Kaolinite as the most common example of dioctahedral two-sheet phyllosilicates has two structures: well or poorly ordered, when viewed by X-ray diffraction. The well-ordered kaolinite, called the T-Kaolinite (the triclinic Kaolinite) has its two-sheet layers arranged above each other in such a manner that there is no movement of these sheets on their axes. The crystals of T-kaolinite, therefore, gives a greater number and sharper reflections in their X-ray diffraction patterns. These are the proof of three-dimensionally ordered crystals. The poorly ordered kaolinite, pM kaolinite, (pseudomonoclinic Kaolinite) has a poor and diffuse X-ray diffraction spectrum. This was caused by the rough structure introduced by the random shift of the individual two-sheet layers along their axes. The halloysite, a member of the two-sheet layer clay mineral, also show shifts of these sheets on their axes. T-Kaolinite is known to reduce plasticity, green strength and dry strength of the clay mineral. However, pM Kaolinite, already considerably delaminated in nature, has an enlarged specific surface area and is noted for its greater ion-exchange, plasticity and greater green and dry strengths. T-Kaolinite is noted for its strong coating property. It is therefore used as an essential constituent of the coating in the paper industry [26].

Chemical treatment involves the treatment of clay with concentrated inorganic acid like HCl or H_2SO_4 or alkaline such as NaOH. These processes results in an increase in the clay specific surface area, porosity and surface acidity [27] 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 [27]. Alkali treatment results in dissolution of the most irregular (amorphous) mineral particles [14]. This alteration was confirmed by X-ray diffraction (XRD) diagrams, where they showed sharpening of the XRD reflection after alkali treatment. However, both acid and alkali treatments can increase variations in surface charge, while the cation exchange capacity (CEC) is altered depending on the types of minerals and treatment methods. Alkali treatment increases the amount of surface groups of intermediate acidity while that of low acidity decreases [28]. Jozefacuik and Matyka-Sarzynska [29] studied the effect of acidification and alkalization on nanopores properties of bentonite, biotite, illite, kaolin, vermiculite and zeolite by well-defined adsorption-desorption isotherms. Report showed increase in specific surface area of the minerals under both conditions. Josefaciut et al [28] studied the acid and alkali treatments of mortmoriolite and kaolinite and reported that the impacts of acid treatment were more pronounced for montmorillonite, while negligible change was observed in the case of kaolinite. However the adsorption capacity of the clay minerals for heavy metals increased generally with acid and alkaline modifications [29].

Adsorption is the most widely used techniques in wastewater treatment process. Activated carbon, silica sand, coal and alumina are usually used as an adsorbent. The effectiveness of an adsorbent depends on the adsorptive properties of their surface. Adsorption takes place when a solid surface is contacted with a solution and tends to accumulate a surface layer of solute molecules created by the unbalance surface forces. Activated carbon have been reported to remove heavy metals such as Pb, Zn, Hg, Cd, Ni, Cu, Cr and Mn [30]. However, from the different types of activated carbon found commercially, very few are selected for heavy metals and are also very costly.

Theory

A very easy and cost effective method of industrial paint effluent treatment based on adsorption has been designed and developed. The approach is feasible in reducing the amount of toxic and heavy metals released into the environment. This method was based on thermal, alkaline and alkaline-thermal treatment for adsorption. In this method, clay samples were calcined at high temperature, treated with alkaline subjected to thermal treatment and used for adsorption of heavy metals present in the industrial paint effluent characterized.

MATERIALS AND METHODS

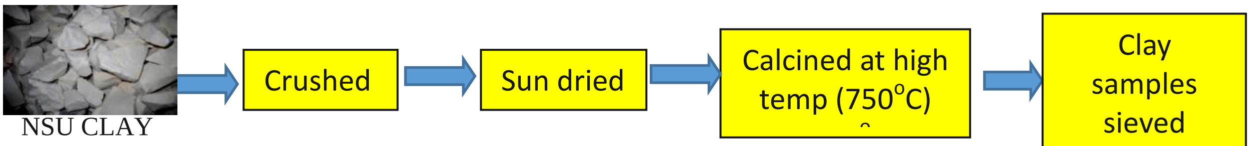
The clay used in this work was sourced from Ehime-Mbano LGA, Imo State, within the South-Eastern region of Nigeria. The paint effluent used was collected from Home Pride Paint Industries, Km 12 Onitsha-Enugu Express Way, Ogbunike, Oyi L.G.A, Anambra State. The following analytical grade chemicals: Sodium hydroxide, ammonium, ethylene di-amine tetra-acetic acid, magnesium sulphate, alkali-iodide acid, phenolphthalein, potassium dichromate, mercuric sulphate solution were used without further purification

Sample preparation

The Nsu clay was crushed, sun-dried, and calcined at high temperature (750 ^oC) for 3 hrs. The clay samples were then sieved through a mesh size of 0.075µm. 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.

Alkaline-Thermal Treatment

The alkaline treatment was carried out in a rotary shaker with temperature and agitation control. The sieved raw clay was treated with NaOH. In this method, 2M and 4M concentrations of NaOH was prepared by dissolving 24g of dry NaOH in 300ml of distilled water and 48g of dry NaOH in 300ml of distilled water respectively. Calculated amount of clay samples (about 300g) was then dissolved in aqueous NaOH. The solution was then transferred into a bowl and then heated on a Magnetic Stirrer Regulator Hot Plate to speed up the reaction. After which the sample was then washed with distilled water, allowed to stand and then the supernatant was decanted. Washing was done repeatedly until the pH was 8. The sample was then subjected to thermal treatment at 100^{o}C for 20 minutes in a furnace. It was then cooled and stored in air-tight plastic bottles.



Small particle size was chosen in order to improve adsorption

Alkaline-Thermal Treatment

Carried out in a rotary shaker with temperature and agitation control.
NaOH of 2M and 4M concentration were prepared.

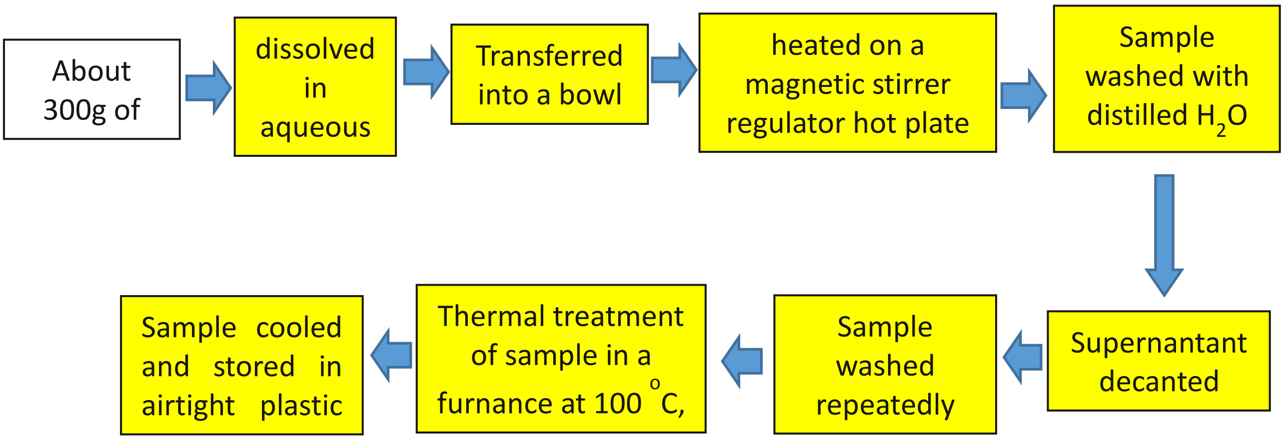


Fig. 4 Flow chart of the sample preparation

Characterization of Clay

The modified clay sample was analyzed for major oxide contents using X-Ray Fluorescence analysis (XRF). In this method, 10g each of the modified clay sample was thoroughly mixed with 2g of stearic acid. The mixture was pressed into a sample pellet using hydraulic pressure press at 20 tons. The sample pellet was analyzed for percentage of major oxides in the clay samples using Minipal 4 Energy Dispersive X-ray Fluorescence spectrometer EDXRF. International standard methods (ASTM) were used to characterize the modified clay for Surface Area (ASTM C1069-09 2014) Specific Gravity/Density (ASTM D 2395-17) and Moisture Content (ASTM D 4643-17)

Characterization of Paint Effluent

The industrial paint effluent sample was characterized for pH, Electrical Conductivity (APHA 2510 2510 B guideline Model DDS-307 (APHA; 1998). Total solids, Total suspended Solids Chloride, Total Dissolved Solids, Turbidity, Biological Oxygen Demand (BOD), Dissolved Oxygen and Heavy Metal were determined using Varian AA240 Atomic Absorption Spectrophotometer (AAS). In Atomic absorption spectrometer's method, the sample was aspirated into the flame and atomized when the AAS's light beam is directed through the flame into the monochromator, and onto the detector that measures the amount of light absorbed by the atomized element in the flame. Since metals have their own characteristic absorption wavelength, a source lamp composed of that element was used, and this made the method relatively free from spectral or radiational interferences. The amount of energy of the characteristic wavelength absorbed in the flame was proportional to the concentration of the element in the sample.

Effluent Sample Preparation

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 residue was completely dissolved. The mixture was cooled, transferred and made up to 100ml using metal free distilled water. The sample is aspirated into the oxidizing air-acetylene flame. When the aqueous sample is aspirated, the sensitivity for 1% absorption is observed.

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.

RESULTS

Table -1 XRF Spectra of Raw and Modified Clay

Composition (%)	Raw Clay	Modified Clay		
		Thermal Treated (Calcination @ 750 ^oC)	Alkaline Treatment (2M NaOH)	Alkaline Treatment (4M NaOH)
SiO_2	57.52	62.00	54.13	52.01
AI2O3	25.29	28.02	22.20	24.22
Fe_2O_3	0.11	0.11	0.24	0.29
TiO_2	0.85	1.93	0.52	0.66
CaO	0.251	0.188	1.26	0.76
MgO	-	-	0.006	-
Na_2O	0.30	0.17	1.38	1.18
K_2O	0.492	0.411	0.547	0.532
SO_3	-	0.130	-	-
MnO	0.0023	0.010	0.028	0.22
Se_2O_3	0.003	0.003	-	-
V_2O_5	0.23	0.130	0.22	0.16
Cr^2O^3	0.079	0.078	0.078	0.075
NiO	-	-	-	-
CuO	0.019	0.016	0.248	0.102
ZnO	-	-	0.358	0.328
BaO	-	0.15	-	-
L.O.I	14.03	6.787	18.79	19.463

Table -2 Characterization of local clay

Parameter	Values
Surface area (m2/g)	32.1
Moisture content (%)	3.0
Specific gravity	2.08
Bulk density (g/ml)	1.94

Table -3 Physicochemical Characterization of the Paint Effluent

Parameters	Experimental 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 µs/cm3	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

Table -4 Physiochemical Analysis of the Paint effluent after clay treatment

Parameters	**Raw Clay**	**Modified Clay**		
		Thermal Treated Clay	**Alkaline Treated Clay**	
			2M NaOH	**4M NaOH**
pH	3.60	3.90	7.46	8.76
Acidity mg/l	187.5	200	95	25
Total Hardness mg/l	610	260	74	46
Alkalinity mg/l	5	12.5	70	185
Oxygen Demand 1	13.5	15.8	12.5	10.5
Chemical Oxygen Demand	149.3	149.3	229.33	288.8
Oxygen Demand 2	6.6	7.8	6.25	7.7
Turbidity NTU	88.9	035	34.8	85.5
Biological Oxygen Demand mg/l	6.7	6.1	5.95	2.8
Total Dissolved Solid mg/l	5.3	0.8	0.2	2.2
Chromium ppm	0.00	0.00	0.00	0.33
Sodium ppm	48.904	10.085	38.644	27.994
Potassium ppm	0.993	0.691	0.875	0.202
Magnesium ppm	28.495	21.762	19.889	1.001
Lead ppm	0.00	0.00	0.298	0.00
Iron ppm	5.263	1.967	1.502	4.988
Silver ppm	0.183	0.001	0.111	0.028
Copper ppm	0.454	0.063	0.102	0.826
Cobalt ppm	0.119	0.118	0.00	0.104
Maganese ppm	0.027	0.228	0.270	0.390

DISCUSSION

Chemical Analysis of Clay

The chemical composition of the kaolinite clay before and after modification was shown in Table 1. From the results it was observed that silica and alumina form the major component of the clay while other elemental oxides were present in minute amount as impurities. The result of the chemical composition of the clay was in agreement with [31]. However, the kaolinite obtained from Ibulu in Delta state Nigeria recorded a higher silica composition of 65.14% and alumina composition of 25.62% [32]. The differences in the composition of the kaolintes may be attributed to environmental factors.

Thermal treatment of the clay lead to an increase in the composition of alumina and silica from 57.52 to 62.0% and 25.29 to 28.02% respectively. The increase might be due to the removal of most of the volatile compounds which led to opening of the pores and exposing the hidden compounds for effective adsorption indicated by the decrease in the loss on ignition from 14.03 to 6.787%. Furthermore, decrease in the composition of alumina may be due to the leaching of 3+2+3+ octahedral cations such as Al, Mg and Fe from the clay by the 3+acids. Alkaline modification of the clay using NaOH exhibited decrease in the silica from 57.52 to 54.13 and then to 52.01 obtained for 2M and 4M NaOH, respectively. The decrease in the concentration of silica was due to the etching reaction between silica and a strong base NaOH used in the modification [14]. Similar results on the decrease in silica to alumina ratio after after alkaline treatment has been reported [14,12].

Characterization of Clay

The specific surface area of a material is a very important property in determining the adsorption capacity of the material. 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. Kaolinite clay usually have a low SA less than 20m/g [33]. However, the SA obtained for Nsu clay was found to be 32.1m2/g kaolin with. This result was in agreement with Chukwujike et al [2] who studied adsorption treatment of industrial paint effluent for the removal of pollutants by local clays. SA of 3m/g was reported by Bhattacharyya and Gupta [34], 10m/g [32] and 19.8m/g [12]. The higher SA of the clay indicates better adsorption of contaminants.

The moisture content of the clay obtained was found to be 3% as shown in Table 2. The low moisture content observed in this study is an indication of improved thermal treatment as evidenced by the rate of evaporation during the treatment. This low moisture content is desirable because more pores was made available for 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 which is a dimensionless unit used to express the ratio of the density of the material to the density of water was determined to be 2.08g/ml. This value was in agreement with Chukwujike, et al [2], and also very close to the literature value of kaolin which has the range of 2.16 – 2.68g/ml expected for kaolinites. The differences may be due to the influence of environmental factors in the location where the clay was collected. The bulk density and specific gravity of which material are closely related. The bulk density of the clay was 1.94g/ml which is very close to the values of 1.97 reported by Baumann and Keller [35] for some kaolinites. 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 [35]. The bulk densities of kaolinites commonly play an important role in its economic value when fired as refractory or adsorbent [2].

Physicochemical analysis of the paint effluent.

The physicochemical analysis of the effluent obtained from the paint industry is shown in Table 3. Most chemical reactions in aquatic environment are controlled by any change in pH making it extremely important. Aquatic organisms are sensitive to pH changes, and biological treatment requires pH control or monitoring. Also the toxicity of heavy metals also gets enhanced at particular pH values. This shows the importance of the pH in determining the quality of a wastewater, and anything higher or lower than the World Health Organization (WHO) limit could be harmful to the environment [36]. From the result it was observed that the pH of the effluent obtained was within the WHO limit of 6.5 – 8.5 (WHO, 2003), which implies that there could be no danger on the receiving environment. The conductivity of water is a measure of the ability of the solution to conduct an electric current. The conductivity of the water is one of the important parameters used to determine the suitability of water for irrigation. It is a useful indicator for salinity or total salt content of effluents. The conductivity of receiving water is simply a function of the concentration of soluble ionic salt present in the effluent. Thus the increase in the salinity of the receiving water body is as a result of high concentration of ionic salts present in the effluent [37]. A value of electrical conductivity greater than 1000μm/cm indicates contamination which is not suitable for aquatic life and the environment in general. The value of conductivity obtained for the paint effluent was far below the WHO standard which indicates a suitable effluent.

The Biochemical Oxygen Demand (BOD) and chemical oxygen Demand (COD) are very useful parameters in accessing the quality of an effluent. The consequences of high BOD and COD are the same as low dissolved oxygen (DO). Both parameters affect directly the amount of DO [2]. 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 to break down into simpler substances, the decomposable organic matter present in any water, wastewater or treated effluent [38]. The greater the decomposable organic matter the greater the oxygen demand and the greater the BOD [39]. 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 of the paint effluent was within the WHO standard while the COD was higher than the WHO limit which may have an adverse effect on aquatic life if the effluent is continuously released into the environment without treatment, leading to a corresponding increase in their receiving water bodies. 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. Effluents usually contains a variety of solid materials. The Total Solid (TS) which is the residue left after evaporation of unfiltered samples were found to be lower than the WHO maximum permissible limit of 50mg/l (WHO, 2003). The solid contained in the filtrate that passes through a filter with a normal pore size of 2μm or less is classified as the Total Dissolve Solid (TDS) [38]. TDS concentration in water is also an important parameter in assessing the quality of water. TDS includes inorganic matter and dissolved materials such as carbonates, bicarbonates, sulphates, chlorides, phosphates and nitrates of calcium, magnesium, sodium, potassium, iron and manganese [40]. A high TDS content affects the density of water, influences osmoregulation of freshwater in organisms, and reduces solubility of gases (like oxygen) and utility of water for drinking, irrigation and industrial purposes [36]. Thus high concentration of TDS in water is not desirable. From the result, TDS concentration of the paint effluent was above the WHO permissible limit of 50mg/l for discharge into potable water bodies. The Total suspended solids (TSS) play an important role in effluent treatment. TSS results are used to assess the performance of a conventional treatment process and the need for effluent filtration in reuse application [38]. TSS is the solid particles under suspension and remains in water samples. The results for TSS for the effluent showed a value higher than the WHO standard limit of 30mg/l (WHO, 2003), which suggest adequate filtration of the effluent before discharge into water bodies.

Total Hardness (TH) is the property of water which prevents the leather formation with soap and increases the boiling point of water. Hardness of water mainly depends upon the concentration of calcium and magnesium salts or both [41]. The effluent from the paint industry recorded a hardness of 700mg/l which is far above the WHO permissible limit of 100mg/l. The increased hardness recorded for the effluent may be attributed to the use of calcium carbonate as additive in paint production. Similarly, the Total Alkalinity (TA) of the effluents was above the WHO maximum permissible limit of 100mg/L (WHO, 2003). A high sulphate concentration of 304.51mg/L and chloride concentration of 600mg/L greater than the WHO limits of 200mg/L was recorded by the effluent. This might have accounted for the high acidity of 185.6mg/L greater than the WHO limit recorded by the effluent.

Excessive chloride in water is not particularly harmful and the criteria set for this anion are based primarily on palatability and its potentially high corrosiveness [42]. Excess Chloride, greater than 200mg/l by WHO imparts salty taste to water and people who are not accustomed to high chlorides may be subjected to laxative effects [2]. Furthermore, high nitrate concentrations are frequently encountered in treated wastewater as a result of ammonium nitrogen and this may lead to eutrophication (OECD, 1992), and methaemoglobinemia in infants and pregnant women [43] above thresholds of 45mg/l concentration. Therefore low concentration of nitrates below 50mg/l set by WHO in any water is required in order to prevent the above mentioned complications. From the analysis the nitrate concentrations of the effluents was within the WHO permissible limit which signifies no danger to the receiving environment.

Heavy Metal Concentration of the Effluents

The concentration of heavy metals in the paint effluent was determined and also presented in Table 3. Heavy metals are toxic at certain concentration, non-biodegradable and bioaccumulate in the food chain which are persistent in nature [13]. From this study, it was observed that calcium, cadmium, sodium, potassium, magnesium, mercury and zinc all showed concentrations within the WHO standard. However, Arsenic, aluminium, chromium, manganese, nickel, copper, lead and iron was higher than the WHO maximum permissible limit, indicating the danger associated with the release of the effluent to the environment. The concentration of iron 10.42 (mg/L) exceeded significantly the WHO permissible limit of 0.3mg/L (WHO, 2003). Similar results on the high concentration of heavy metals in effluents have also been reported [44,45]. Consequently, in order to avoid these complications associated with high metal concentrations, the paint effluent was treated in order to get rid of these metals or reduce their concentrations to permissive levels.

Treatment of the Paint Effluent

The effluent was treated with modified Nsu clay to reduce these parameters to acceptable limits. The unmodified raw modified clays were utilized for the effluent treatment. The results obtained from these three different clay modification were compared (Table 4)

Total Alkalinity

The total alkalinity of the paint effluent decreased significantly when treated with the clays to acceptable limits to conform to WHO standard. The raw and calcined clays were observed to decrease drastically the concentration of the total alkalinity when compared to the initial concentration in the paint effluent. On the contrary, the alkaline treated clays were not effective in the treatment of the alkalinity of the paint effluent. The alkalinity of the effluent treated with 4M NaOH-C increased further from 165 to 185mg/L.

Total Hardness

The alkaline treated clay was the most effective in the reduction of the total hardness. This was seen by the decrease to WHO acceptable limits below 100mg/L for the alkaline treated adsorbents, although all the clays recorded a decrease in the total hardness of the effluent after treatment.

Total Acidity

The effluent treatment with 4M-NaOH clay exhibited the best result as seen in Table 3 where a significant reduction in the acidity from 185.6 to 25mg/L was recorded which was below the maximum WHO permissible limit of 100mg/L. The result indicates that alkaline treatment is the best foe acid reduction in industrial paint effluent.

COD and BOD

The chemical oxygen demand (COD) of the effluent decreased significantly when treated with the all the prepared clay samples. However, the values were still higher than the WHO maximum permissible limit of 40mg/L. The raw and calcined clays recorded the greatest decrease in the COD of the effluents, probably because no chemical was utilized in the clay treatment which could contribute to the COD of the effluent. A decrease in the BOD of the effluent was also obtained after various clay forms were utilized for treatment, with the best treatment obtained for the 4M NaOH-C.

Heavy metals Treatment

A decrease in the concentration of all the metals in the paint effluent was observed when treated with all the prepared clay samples. However, manganese and iron showed a decrease, but were still higher than the WHO maximum permissible limit. Many researchers have reported a decrease in heavy metal concentration from contaminated solutions after clay treatments [34, 40]. Comparing the treatment potential of the clays for the paint effluent, the 4M-NaOH-C was found to be more effective for the reduction in potassium magnesium and cobalt. Moreso, the calcined clay was generally found to be more effective for the treatment of the heavy metals than the other clay samples.

Iron

There was an observed decrease in the iron concentration of the paint effluent after treatment with the clay samples prepared. The calcined and 2M NaOH 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 1.502mg/L, respectively. However, the iron concentration was still higher than the recommended WHO limit of 0.3mg/L. More adsorption mechanisms should be adopted in order to reduce the iron concentration on the paint effluent.

Silver

The study showed high reduction in the silver content of the effluent when treated with the prepared clay samples. This is an indication that Nsu clay is an excellent adsorbent for silver ions as evident from the effective reduction in the concentration of silver in the effluent from 6.543 to 0.183 when treated with raw clay.

Copper

The study showed great reduction in the copper concentration of the effluent when treated with all the prepared clay samples. The calcined and 2M NaOH clay were observed to be the best adsorbent for the removal of copper from the effluent with a high reduction from 2.49mg/L to 0.063 and 0.102mg/L, respectively. However, the copper concentration was lower than the recommended WHO limit of 1.0mg/L.

CONCLUSION

A very simple, cost effective and economically feasible method of adsorption of pollutant from industrial paint effluents using modified clay has been developed and studied. The treatment of toxic pollutant discharged by the paint industries has become a major problem due to stability and non-degradability of these compounds. One of the key technical problems associated with the use of natural clays is that they have low adsorption capacity when compared with activated carbon. To overcome this problem, thermal and alkaline activations were carried out on the kaolin clay. High adsorption was achieved when the surface and the adhesion properties of the clay was enhanced by thermal and alkaline treatment at high temperature (750^{o}C) and by combination of thermal and alkaline activation. The clay used in this study has proved to be suitable adsorbent for the treatment of industrial paint effluent as evident by more than 60% reduction in concentration of both the heavy metals and other toxic pollutant present in the industrial paint effluent studied.

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