Characterization Adsorption and Antibacterial Properties of Silver-Modified Kaolinite Clay from Kwi, Plateau State Nigeria

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Abstract

Clay samples from Kwi, Barkin Ladi Local Government Area of Plateau State, Nigeria was purified and characterized using XRF, FT-IR and XRD. Silver-modified clay was prepared in order to develop an antibacterial and adsorptive material. The modified and purified clays were tested for antimicrobial activity against Staphylococcus aureus, Enterobacteriae, pseudomonas aureus and salmonella typha by microbiological test as well as adsorptive properties against Chromium (III), Nickel (II), and Lead(II) from leather ternary effluent. From the results the silica content (SiO₂) was found to be 56.12%, followed by alumina (Al₂O₃) 23.90%, iron (III) oxide 2.31% among others. The X-Ray diffraction studies showed that the clay deposit consist predominantly of kaolinite with d-spacing of 7.14639Å and 3.57632Å respectively and traces of quartz with d-spacing of 3.34520Å as well as orthoclase. The FT-IR spectral analysis of the clay samples reveals wave number and absorption band at 3688.02 and 3618.58cm⁻¹ which arise from the internal surface OH group indicative of kaolinite and also deformation band at 1003.02 and 910.43 cm⁻¹. Results have shown a strong antimicrobial activity of the Ag modified clay, which considerably inhibited the growth of ordinary microorganisms, including Gram-positive and Gram-negative bacteria. The Ag-clay reacted positively to organisms that had hitherto shown resistance to common antibiotic drugs. Also upto 64% of Cr ions and 94% of Ni ions were removed from ternary wastewater by Ag-modified and purified clays respectively. The results have confirmed the strong anti-bacterial activity of Silver ion. Keywords: Clay characterization, adsorption, anti-microbial Properties, ternary wastewater

DOI: 10.7176/CMR/13-1-04

Publication date: January 31st 2021

1.0 INTRODUCTION

Clay is a term used to describe either the size of the individual particles present in a deposit or the specific minerals of a size less than 0.002mm in dimension (Fábio *et al*, 2009; Nwosu *et al*, 2013 and Abuh *et al*, 2014). Understanding the distinction between clay size and clay minerals is important because two samples of clay having identical particle size may have varying behaviours based on the clay minerals present (Gray *et al*, 2013). As a result of the substantial differences in behaviour of the various types of clay minerals, determining the type and proportion of clay minerals in a particular clay deposit is one of the first and most important steps necessary in screening a source material.

The application of nanotechnology in the purification and treatment of wastewater may potentially revolutionize water treatment processes (Zhang, 2006; Vishnu and Bibi 2013; Gil *et al*,2011; Bhattacharya *et al*, 2013). Characteristics such as large surface area, high specificity, high reactivity, catalytic potential and the absence of internal diffusion resistance make nano-particles excellent candidates for water treatment applications (Bergaya *et al*, 2006). According to Vishnu and Bibi (2013), nanoscale has stimulated the development and use of novel and cost effective technologies for remediation, pollution detection and pollution monitoring.

Among natural available nanoporous materials, clay minerals have several important advantages over alternative adsorbents. Clays are inexpensive, abundantly available and non-toxic, and have good sorption properties and ion exchange potential for charged pollutants. (Gil *et al*,2010). Clays possess a wide range of pore size distribution ranging from micro to mesopores (Haydel *et al*, 2008). Added to these is the fact that clay mineral platelets are truly nano-particulate and usually have very large surface area in the region of between 10 and 700m²/g together with its multifunctional properties. The second is the fact that clay mineral's expansive surface often has an electrical charge that results in accumulation of inorganic and organic cations; coupled with its availability, low cost and ease of modification, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC) (Falkinham *et al*, 2009). Thirdly, incorporation of various species and nanoparticles into the interlayer space allows clay minerals to be utilized as new functional materials (Li *et al*, 2002; Oya *et al*, 1991). These clay based functional materials and nano-composites demonstrate a great variety of applications such as adsorption and environmental remediation due to their variety in structural and surface properties, high chemical stability, high specific surface area and high adsorption capacity (Bergaya *et al*, 2006). Such features allow the clays to be tailored to suit specific decontaminating purposes which can bring about considerable advantages from industrial application point of view (Haydel *et al*, 2008).

Living Clay is known to have been used historically as an effective antibacterial in the treatment of dysentery, and as a means of decontaminating water. Presently it is being used internationally to clarify and balance small

and large bodies of water. This is so because Living Clay particles are smaller than many bacteria; when bacteria encounter an environment abundant in clay it becomes surrounded by the clay, and are imbedded in it. The immediate result is that the bacteria are unable to receive nourishment and cannot survive (Haydel *et al*, 2008.

A recognized detoxifying agent, nutrient and bactericidal Calcium Montmorillonite Clay is in the smectite group of clays. Its power as a detoxifying substance comes from its inherent ability to adsorb and absorb. Its unique ability to grow and adsorb is the reason for its classification and recognition as a Living Clay (Haydel *et al*, 2008 While there is more than one Montmorillonite, the red Calcium Montmorillonite Clay of the smectite group remains a favourite for human use. For example, Iron-rich smectite and illite clay (Montmorillonite/Bentonite type of clay) is effective in killing bacteria *in vitro*. The authors reported that the clay mineral exhibited bactericidal activity against *E. coli*, ESBL (Extended-Spectrum Beta-Lactamases); *S. enterica serovar Typhimurium, P. aeruginosa*, and *M. marinum*, and significantly reduces grown without added mineral products (Haydel *et al*, 2008). Similarly, Falkinham et al. (2009) have also studied the antibiotic and antimicrobial activity of red clays is likely due to the proliferation of antibiotic-producing bacteria, which is induced by the clay.

Antimicrobial materials are classes of materials that have the ability of inhibiting the growth or even killing some kinds of microorganisms. This property is very important at certain industry segments, normally those that require large purity and hygiene, along with a partial or complete removal of noxious microorganisms (Li *et al*, 2002

Researches have shown that montmorillonites intercalated with metallic ions with bacteriostatic nature, such as silver, copper, zinc, mercury, tin, bismuth, cadmium, chromium and thallium provide a strong antimicrobial activity to the clay (Oya *et al*, 1991; Ohashi and Oya, 1992; Zhou *et al*, 2004). . It has been shown that these ions can inhibit birth and growth, or even kill harmful microbes, by altering the metabolisms of bacterium and fungus (Hu and Xia, 2006; Frost *et al*, 2006).

Clay minerals may be administered either orally as antacids, gastrointestinal protectors, anti-diarrhoeic, osmotic oral laxatives, homeostatic, direct emetics, antianemics and mineral supplements, or parentally as antianemics and haemostatics. They may also be used topically as antiseptics, disinfectants, dermatological protectors, anti-inflammatories, local anaesthetics and keratolytic reducers (Carretero and Pozo, 2010).

Inorganic antibacterial products are usually in the form of a composite, in which the metallic ions are impregnated in or covered on a carrier (Li *et al*, 2002). Silver ions are extensively used in the synthesis of antibacterial agents because it is a very effective specimen in killing bacteria, at relatively low concentrations, and with a low toxicity. In water treatment and food industry, silver as antimicrobial agent is considered safer and relatively inert, and consequently, the most appropriate for such applications (Oliveira and Oliveira, 2004).

This work reports the results of the characterization, antibacterial and adsorption properties of silver modified clay from Kwi, Plateau State, Nigeria.

2.0 MATERIALS AND METHODS

Clay samples were obtained from Kwi, Barkin Ladi Local Government Area of Plateau state, Nigeria. The wastewater used for this work was collected from Naraguta Leather Work, Jos North Local Government Area of Plateau State, Nigeria.

2.1CLAY PURIFICATION

The clay samples were crushed and dispersed in a plastic container with large volume of water. The clay was then filtered to remove stone and the filtrate was allowed to sediment for 24hours. The clay was re-suspended in water again and allowed to stand overnight. The top fraction was removed and purified as follows. The clay obtained was re-dispersed in de-ionized water and heated at 75°C in the presence of solutions containing sodium salts of bicarbonate (1M), citrate (0.3M) and chloride (2M) as described by Mecabih and Bouchikhi [22]. This process will eliminate organic and inorganic compounds including Al, Fe, and other free cations.

Carbonates in the clay were removed by treatment with 0.5M HCl; this was followed by treatment with 30% v/v H₂O₂ at 70°C to remove all organic matter. After several washings with water to remove chloride, the sample were treated with 1M NaCl to convert the clay to its Na⁺ form to enhance swelling before drying at 110°C. This sample was labeled purified clay (PC). The purified clay was subjected to XRF, FT-IR and XRD analyses to ascertain the nature and composition of the clay.

2.2PREPERATION OF SILVER MODIFIED CLAY

Silver modified clay was prepared by adding 6.0g of sodium hydroxide (NaOH) into 125ml of deionized water followed by 3g of silver nitrate (AgN0₃) with constant stirring until all the silver nitrate has dissolved. About 10g of purified clay was added in to AgNO₃/NaOH solution and aged for 72hours. It was then filtered and calcined at

 400^{0} C for 2hours, pounded in to powdered form by the use of glass mortar. This sample was labeled silver modified clay.

2.3ADSORPTION STUDIES

In adsorption studies, 2g of each of the sample clay was added into 100ml of wastewater separately and was allowed to stand for 2hours, the clay were filtered out and the water was analyzed in each case, for the purified clay and silver modified clay by the use of atomic adsorption spectrophotometer.

Removal efficiency (%) =
$$\frac{C_0 - C_f}{C_0}$$
 x $\frac{100}{1}$

Where C_o and C_f are the initial and final concentration of the metal ion (mg/L) in the wastewater.

2.4ANTIMICROBIAL STUDIES

The wastewater sample was taken to Department of Microbiology, University of Jos for microbial count and susceptibility test before and after treatment with the clay samples. Bacterial identification test includes; catalase test for streptococci, coagulase test for staph aureus, citrate utilization test for entero-bacteria, indole test for gram negative bacilli, oxidase test for pseudomonas and gram staining which is a method of differentiating bacteria species into two large groups (gram positive and grain negative).

2.5Characterization of Clay Samples

3.0PRESENTATIONOF RESULTS

3 1CHARACTERIZATION OF KWI CLAY

X-Ray Fluorescence Spectrophotometer (XRF) and X-Ray Diffraction Spectrophotometer (XRD) was made available by National Geological Research Agency (NGRA), Kaduna, Nigeria while Fourier Transform Infra-Red Spectroscopy (FT-IR) was made available by National Research Institute for Chemical Technology (NARICT), Zaria Nigeria.

Table 1. XRF RESULT ANALYSES FOR KWI CLAY				
OXIDES COMP.	%			
SiO ₂	56.12			
TiO ₂	1.58			
Al ₂ O ₃	23.90			
Fe ₂ O ₃	2.31			
CaO	0.28			
MgO	0.17			
Na ₂ O	1.287			
K ₂ O	1.863			
MnO	0.01			
V_2O_5	0.22			
Cr_2O_3	0.199			
NiO	0.02			
CuO	0.059			
ZnO	0.059			
SrO	0.13			
BaO	0.85			
PbO	0.045			
L.O.I	10.89			

The results of the XRF analysis of Kwi clay is shown on Table 1. The result shows the major constituents of the samples to be silica and alumina. Other elemental constituents' present includes Na_2O , Fe_2O_3 , TiO_2 , and K_2O . The 56.12% SiO₂ and 23.90% of Al₂O₃ suggest that the clay sample belongs to the kaolinite family.



Fig 1: XRD pattern of Kwi clay

Pos.[°2Th.]	Height [cts]	EWHMLeft[°2Th.]	d-spacing[Å].	Rel. Int. [%]	Clay Type
12.3860	2873.57	0.1023	7.14639	90.28*	Kaolinite
24.8976	3182.92	0.1279	3.57632	100.00*	Kaolinite
26.6484	2522.22	0.1023	3.34520	79.24*	Quartz

Table 2: TOP 3 PEAK LIST OF THE XRD RESULT

3.2 X-RAY DIFFRACTION (XRD) OF KWI CLAY

XRD measurements were employed to determine the mineral present in the clay sample (Figure1 and Table 2). It was found that the main mineral in the clay sample was kaolinite and quartz. With a principle reflection of Kaolinite having $2\theta_{CuKa} = 12.3860$ °2Th., d-spacing = 7.14639Å, Rel. Int. = 90.28% and $2\theta_{CuKa} = 24.8976$ °2Th., d-spacing = 3.57632Å, Rel. Int. = 100% and quartz at $2\theta_{CuKa} = 26.6484$ °2Th., d-spacing = 3.34570Å and Rel. Int. = 79.24% and other pattern were observed which indicate other mineral in small fractions are present in the clay sample.

3.3 FT-IR RESULTS FOR KWI CLAY



Figure 2: FTIR Spectra of KWI Clay

Table 3: Major bands and Assignment in Kwi Clay

Peaks	Assignment			
640.39	Si-O			
678.97	Si-O perpendicular			
748.41	OH bending towards the surface of clay sheet			
786.98	Si-O			
910.43	AlAlOH deformation			
1003.02	in plane Si-O stretching			
1111.03	stretching vibrations of Si-O bonds			
1651.12	OH deformation of water			
3618.58	Stretching vibrations of surface hydroxyl groups for kaolin			
3688.02				

The spectrum in figure 2 demonstrates well crystalline kaolinite. The sharp doublet at 3688.02 and 3618.58 cm⁻¹ is characteristic for the kaolin group in general. The bands at 3688.02 cm⁻¹, and near 3618.58 arise from the internal surface OH groups. The OH deformation bands of kaolinite are situated at 1003.02 and 910.43cm⁻¹. Supporting bands at 786.98 (Si-O) and 678.97 cm⁻¹ (Si-O) are diagnostic for kaolinite.

3.4ADSORPTION OF METAL IONS

The results and comparison of the concentrations in mg/L of Chromium (II), Cadmium (II), Lead (II), and Nickel (II) found in Leather Works waste effluent before and after adsorption with Ag-modified as well as purified clay are reported in tables 4and 5 below.

TABLE 4: Concentrations of Chromium (III), Lead (II), and Nickel (II) in Tannery Wastewater before and after treatment with purified Kwi clay

HEAVY METALS	Cr^{3+}	Pb^{2+}	Ni ²⁺	Cd^{2+}
Initial metal concentration (mg/L)	0.0629	0.9298	0.1483	ND
Final metal concentration (mg/L) after treatment	0.0503	0.8759	0.0079	ND
Amount removed (mg/L)	0.0126	0.0539	0.1404	ND
Removed efficiency	20.03%	5.79%	94.67%	ND

 $Ni^{2+}>Cr^{3+}>Pb^{2+}$

TABLE 5: Concentration of Chromium (III), Cadmium (II), Nickel (II) and Lead (II) found in Tannery wastewater before and after treatment with silver (Ag) modified Kwi clay.

HEAVY METALS	Cr ³⁺	Pb^{2+}	Ni ²⁺	Cd^{2+}
Initial metal concentration (mg/L)	0.0629	0.9298	0.1483	ND
Final metal concentration (mg/L) after treatment	0.0226	0.8624	0.1191	ND
Amount removed (mg/L)	0.0403	0.0674	0.0292	ND
Removed efficiency	64.06%	7.24%	19.68%	ND

 $Cr^{3+}>Ni^{2+}>Pb^{2+}$ NB: ND means not detected

3.5ANTI-BACTERIAL STUDIES

The total microbial count (TMC) and identification in raw leather works wastewater as well as the Biochemical and Susceptibility test results, the Drug Abbreviations and Full names in susceptibility test are shown in tables 6-**Table 6: Microbial count and identification in Leather works wastewater**

		Waste Water Before	After Treatment with	After Treatment
S/N		Treatment	Purified Clay	with Silver
		(Raw water)		Modified Clay
	Total plate	106	96	16
1	Microbial count			
	Coliform count	76	33	12
2	Identified micro-	Staphylococcus aureus, E.	Staphylococcus aureus,	E. coli, proteus
	organisms present	coli, proteus spp,	Enterobacteriae, E. coli	spp
	in raw and treated	Enterobacteriae,		
	wastewater.	pseudomonas aureus		
		salmonella typha		
3	Gram Reaction	Gram positive cluster, gram	Staphylococci aureus,	Gram negative
		negative short rods, gram	Gram negative short rods,	short rod, Gram
		negative long rods, gram	Gram positive rod, Gram	positive rods
		positive rods	negative long rods	



Table 7: Biochemical Test Results

S/No	Sample	Catalase	Cuagulase	Indole	Citrate	Oxidaze	Motility	Glucose	Lactose	Sucrose	Triple sugar ion agar slant butt slope gas H ₂ s
1	Waste water sample	+	+	+	+	+	+	+	+	+	Y Y + +
2	After treatment with purified clay	+	+	+	+	-	+	+	-	-	R Y
3	After treatment with silver modified clay	-	-	+	-	-	+	+	-	-	R Y

NB: YY means glucose, lactose and sucrose are fermented RY means only glucose fermented

Table 8: Susceptibility test

		ANTI-BIOTICS D	ISC ON MICRO-ORGANISM ISOLATED	
S/NO	Sample	Organism	Sensitive	Resistant
		Pseudomonas	CPX, AU, CN, PEF, OFX, CEP, PN, S	NA
1		E.coli	SXT, AU, CN, S, CPX, OPX	PEF, NA,
	Raw Waste Water			PN, CEP
		Staphylococcus	CN, PEF, SXT, S, CPX, R	APX, Z,
		aureus		AM
		Bacillus spp	CPX, R, AMZ, APX, CN, PEF, S	SXT, E
		Proteus spp	CPX, SXT, S, PN, CEP, OFX	AU, CN,
				PEF, NA
		Staphylococcus	SXT, E, PEF, CN, R, CPX	APX, Z,
2	After Treatment	aureus		AMS
	with Purified clay	E. coli	SXT, S, PN, CEP, NA, PEF, CN, AU,	
			CPX	
		Enterobacteriae	SXT, E, PEF, CN, APX, Z, AM, R, CPX	
		Proteus spp	CPX, SXT, S, PN, CEP, OFX	
3	After Treatment	E. coli	CPX, SXT, S, PN, OFX, NA, PEF, CN,	
	with Silver modified		AU	
	clay			

Gram Negative	e Rods	Gram Positive Rods		
OFX	TARIFID	PEF	PEFLACINE	
PEF	PEFLACINE	CN	GENTAMYCIN	
CPX	CIPROFLOX	APX	AMPICLOX	
AU	AUGUMENTIN	Ζ	ZINNACEF	
CN	GENTAMYCIN	AM	AMOXACILIN	
S	STREPTOMYCIN	R	ROCEPHIN	
CEP	CEPOREX	CPX	CIPROFLOXACIN	
NA	MALIDIXIC ACID	S	STREPTOMYCIN	
SXT	AMPICILIN	SXT	SEPTRIN	
		Е	ERYTHROMYCIN	

Table 9: Drug Abbreviations and Full names in susceptibility test

4.0DISCUSSIONS

4.1ADSORPTION PROPERTIES: The initial concentration of the heavy metals (Cr, Ni, and Pb) in Naraguta leather works waste effluent were analyzed to be 0.0629, 0.1483 and 0.9298mg/L respectively as shown in Table 4 above, which significantly decrease to 0.0503, 0.0079 and 0.8759 respectively after treatment with purified clay with a removal efficiency of 20.03%, 94.67% and 5.79%. Cadmium (Cd) was not detected in the water sample. This could be attributed to its presence in concentration below the detection limit of the instrument used. There was a high preference of Ni for the purified clay than other metal ions. As seen inTable 5, the concentration of Chromium (II), Nickel (II), and Lead (II) also decreased to 0.0226, 0.1191and 0.8624 after treatments with silver (Ag) modified clay which showed a removal efficiency of 64.06% for Chromium (II), 19.68% for Nickel (II) and 7.24% for Lead (II) respectively. The concentration of heavy metal decreased significantly in the treated wastewater when compared to the untreated water. The result also showed that purified clay had higher affinity for Ni²⁺ while silver modified clay had higher affinity for Cr³⁺.

According to Bineesh and Park (2011), when the exchangeable cations in clay are replaced by polymeric and oligomeric hydroxyl metallic cations, calcined at 300-500°C, a pillared clay with a stable pillar having increased inter-layer spacing possessing micro-pores capable of strong adsorption is formed. Gil et al. (2010) have also reported that pillaring improves the structural characteristics of the clay, increasing the accessibility of the reactant molecules to the interlayer active sites. These classes of materials possesses shape-selective properties due to their inter-layer and inter-pillar distances which control the diffusion rates of reactants, reaction intermediates and products according to Molina et al (2011). Similarly, Enoh and Wetpan (2015) have demonstrated that the modification of clay using acid enhanced the adsorption of metal ions from water by removing between 57 -100% of metal ions studied. According to Basak et al(2012), isomorphic substitution within the clay layer by Mg²⁺, Fe³⁺/Fe²⁺ or Al³⁺ generates negative charges that are normally counterbalanced by hydrated alkali or alkaline earth cations (Na⁺, K⁺, Ca²⁺, etc.) residing in the interlayer. Because of the relatively weak Van der Waals forces existing between the layers, intercalation of various molecules is feasible. This is the basis of the adsorptive properties of silver and other modified clays.

4.2ANTIMICROBIAL PROPERTIES

Table 6 shows the microbial count, microorganisms that were present in raw wastewater and the gram reaction of bacterial. The total plate count and coliform count of micro-organic before treatment were 106 and 76, which reduces to 96(9.43%) and 33(56.6%) after treatment with purified clay and 16(84.9%), 12(84.2%) after treatment with silver modified clay. Also the identified micro- organisms that were present in the wastewater include: Staphylococcus aureus, pseudomonas, enterobacteria, proteus spp, E.coli and salmonella typhi which reduces to staphylococcus aureus, enterobacteria, E.coli after treatment with purified clay, and after treatment with silver modified clay reduced to proteus spp and E.coli only. According to the result, there were Gram positive cluster, Gram negative short rods, Gram negative long rods and Gram negative long rods after treatment with purified clay. Treatment with silver modified clay reduced the micro- organism to Gram negative short rod and gram positive rod sonly.

Table 7 shows Biochemical test of the micro-organism before and after treatment with purified and silver modified clay. The wastewater gave a positive test for catalase (staphylococcus), oxidase (pseudomonas), motility, glucose, Lactose, sucrose, while after treatment with purified clay it gave a negative test to oxidase, lactose, sucrose and treatment with silver modified clay give a negative test to catalase, coagulase, citrate, oxidase, lactose and sucrose.

Table 8 shows susceptibility test of the micro- organism which is all about sensitivity and resistant of microorganism before and after treatment of wastewater with purified and silver (Ag) modified clay. From the results, all the micro-organisms found in the raw wastewater showed high sensitivity to most of the common antibiotic drugs and resistance to some few drugs. However, after treatment with purified clay, only Staphylococcus aureus showed resistance to three of the drugs (APX, AM, Z) while others were sensitive to all the other drugs tested. The ability of raw clay to remove micro-organisms from water have been attributed to the presence of Iron(III) ions (Haydel *et al*, 2008). Similarly, after treatment with silver modified clay, the two micro-organisms identified were sensitive to all the drugs tested and there was no resistance. This further confirms that silver-nanoclay could serve as a strong and potent antibiotic drug especially in areas where resistance to common drugs have been reported, although more research is required to ascertain the effect of this type of material in humans. This claim is supported by the work of Shalini *et al.* (2012) who reported that Silver (Ag) nanocatalyst is highly efficient for the degradation of microbial contaminants in water and are reusable as well. It is important to note that heating the clay to a temperature of 400°C ensures that every form of micro-organisms that were present inside the clay was destroyed.

Clay's ability to attract toxins, bacteria, heavy metals, and other noxious substances have been reported to come from its positive electrical charge (Haydel et al, 2008). With toxic and unhealthy substances tending to have a negative electrical charge, they are irresistibly attracted to the radiantly positive pole of the clay. Nano-Ag is currently the most widely used antimicrobial nanomaterial. Its strong antimicrobial activity, broad antimicrobial spectrum, low human toxicity, and ease of use make it a promising choice for water disinfection and microbial control. It is now well accepted that the antimicrobial activity of nano-silver largely stems from the release of silver ions (Xiu et al., 2011, 2012). Also, as the size of silver particles decreases to the nano-scale, their antibacterial efficiency increases due to their large surface area per unit volume. Silver ions generated from the silver surface bind to the reactive group in the target cell or organism, resulting in their precipitation and inactivation. The destruction of bacterial life is dependent on the physical-chemical factors that affect the ability of a cell to grow and multiply. Antimicrobial agents either inhibit growth (bacteriostatic) or destroy cells (bactericidal). The most important factors for impeding bacterial viability are temperature, pH, osmotic pressure, oxidation state, and concentrations of nutrients and wastes (Nolte, 1982). Homeostasis (internal stability) of the cell depends on the action and interaction of a number of physiological systems, and therefore, the effect of the clay mineral surface and related aqueous solution chemistry on the functioning of the whole cell must be considered. Bactericides function by impeding nourishment, disrupting essential metabolic activities, suffocation (precipitation of a solid phase rendering the cell wall impermeable), poisoning (delivery of a toxin), or physical disruption (cell lysis by bursting or penetration) (Nolte, 1982).

5.0CONCLUSION

Although natural clay possesses antibacterial properties, the study have shown that the purification of clay and the introduction of silver ion into clay inter-layer enhances its adsorptive and anti-bacterial properties. The research has demonstrated that silver modified clay has a broad-spectrum in vitro antibacterial activity against antibiotic-susceptible and antibiotic-resistant bacterial pathogens and could be used for such purpose especially given the fact that antibiotic resistance is on the rise in most developing countries, the need for new therapies to combat dangerous bacterial infections cannot be over emphasized. This could be exploited in several products such as paint, cream, and powder.

6.0REFERENCES

- Abuh, M. A.; Abia Bassey N.; Udeinya, T. C.; Nwannewuihe, H. U.; Abong, A. A.; and Akpomie, K. G.(2014): Industrial Potential off Adiabo clay in Calabar Municipal of Cross River State, South-South Nigeria. Pac. J. Sci. Tech. 15(1): 63-75.
- Basak ,B. B., Sharmistha Pal1, and S. C. Datta(2012): Use of modified clays for retention and supply of water and nutrients. CURRENT SCIENCE, VOL. 102, NO. 9, 10 MAY 2012, 1272-1278.
- Bhattacharya, Sayan; Indranil Saha; Aniruddha Mukhopadhyay; Dhrubajyoti Chattopadhyay; Uday Chand Ghosh and Debashis Chatterjee(2013): Role of nanotechnology in water treatment and purification: Potential applications and implications. International Journal of Chemical Science and Technology 2013; 3(3): 59-64 Available online at http://www.urpjournals.com
- Bergaya F, Theng BKG, Lagaly G, editors.(2006): Handbook of Clay Science, Developments in Clay Science. Vol. 1. Elsevier Ltd; Amsterdam: 2006. pp. 717–741. ISBN 0-08-044183-1 p. 723.
- Bineesh, K. V. and Dae-Won, Park(2011):Structural Modification of montmorillonite clay by Pillaring process: Its Characterization and applications. In: Clays: Types, Properties and Uses. Ed. By J. P. Humphrey and D.E. Boyd, Nova Science, Pub. P372- 392.
- Carretero M.I. and Pozo, M.(2010): Clay and non-clay minerals in the pharmaceutical and cosmetic industries Part II. Active ingredients, Applied Clay Science 47: 171-181 (2010).
- Enoh. B. S. and C. Wetpan(2015): Adsorption of Metal Ions from Carwash Wastewater by Phosphoric Acid Modified Clay: Kinetics and Thermodynamic Studies. Chemistry and Materials Research Vol.7 No.4, 2015 pp1-8, www.iiste.org. ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online).

Fábio Luiz, Melquiades, Fábio Lopes, Susana M. S, Mônica R, Paulo S., Parreira, Carlos

- R. A (2009). Chemical characterization of clay SRM by X-ray florescence results comparison from different laboratories, Ciências Exatas e Tecnológicas, Londrina, v. 30, n. 2, p. 145-150.
- Falkinham Jo,; Wall, T.; Tanner, J.; Tawaha, K.; Alali, F.; Li, C.; Oberlies, N. (2009): "Proliferation of antibioticproducing bacteria and concomitant antibiotic production as the basis for the antibiotic activity of Jordan's red soils.". Applied and environmental microbiology 75 (9): 2735–2741. doi:10.1128/AEM.00104-09.
- Feng, Q.L., Wu, J., Chen, G.Q., Cui, F.Z., Kim, T.N., Kim, J.O., (2000): A mechanistic study of the antibacterial effect of silver ions on Escherichia coli and Staphylococcus aureus. Journal of Biomedical Materials Research 52 (4), 662 to 668.
- Frost R., He H., Yang D., Yuan P., Shen W., (2006): A Novel Organoclay with Antibacterial Activity Prepared from Montmorillonite and Chlorhexidini Acetas, Journal of Colloid and Interface Science 297, 235-243.
- Gray, M.; Neerdael, B.; and Degnan, P.(2013): Characterization of swelling clays as component of the Engineered Barrier System for Geological repositories. IAEA, Vienna International Centre, Austra. www: pub.iaea.org.
- Gil, A.; Korili, S. A.; Trujllano, R. and M. A. Vicente(Eds) (2010): Pillared Clays and Related Catalysts. Springer, Nueva Pub. New York. Pp343-354.
- Gil, A., Assis, F. C. C., Albeniz, S., and Korili, S. A. (2011). Removal of dyes from wastewaters by adsorption on pillared clays. *Chemical Engineering Journal*, 168, 1032-1040.
- Haydel, S.; Remenih, C.; Williams, L. (2008): "Broad-spectrum in vitro antibacterial activities of clay minerals against antibiotic-susceptible and antibiotic-resistant bacterial pathogens.". The Journal of antimicrobial chemotherapy 61 (2): 353–361. doi:10.1093/jac/dkm468. PMC 2413170. PMID 18070832.
- Hu C. and Xia M.,(2006): Adsorption and Antibacterial Effect of copper-exchanged montmorillonite on *Escherichia coli* K88, Appl. Clay Sci. 31, 180-184.
- Li B., Yu S., Hwang J., Shi S.,(2002): Antibacterial Vermiculite Nano-Material, Journal of Minerals & Materials Characterization & Engineering 1, 1, 61-68.
- Liau, S.Y., Read, D.C., Pugh, W.J., Furr, J.R., Russell, A.D., (1997): Interaction of silver nitrate with readily identifiable groups: relationship to the antibacterial action of silver ions. Letters in Applied Microbiology 25 (4), 279-283.
- Mecabih, Z., Kacimi, S. and B.Bouchikhi(2006):Adsorption of Organic matter from Urban Wastewater on Bentonite Modified by Fe(III), Cu(II) and Al(III), Rev. Sci. Eau Vol.19, No1, pp23-31
- Molina, C. B.; Casas, J. A.; Pizarro, A. H. and J. J. Rodriguez (2011): Pillared Clays as Green Chemistry Catalysts: Application in Wastewater Treatment. In Clays: Types, Properties and Uses. Edited by J. P. Humphrey and D. E. Boyd. Nova Science Pub.pp 435-474.
- Nwosu D.C., Ejikeme P.C.N., and Ejikeme Ebere M (2013). Physic-Chemical Characterization of "NGWO" White Clay for Industrial Use. International Journal of Multidisciplinary Sciences and Engineering, Vol. 4, NO. 3, availble online at www.ijmse.org.
- Nolte W. A.(1982): Oral Microbiology. 4. Mosby; London: 1982. pp. 3–37 Oliveira L. and Oliveira P.(2004): Review: Main Antimicrobial Agents Used in Plastic Packaging, Braz. J. Food Technol. 7, 2, 161-165 (in Brazilian Portuguese).
- Oya A., Banse T., Ohashi F., Otani S., (1991): An antimicrobial and antifungal agent derived from montmorillonite, Appl. Clay Sci. 6, 135-142.
- Ohashi F. and Oya A.,(1992): Antimicrobial and antifungal agents derived from clay minerals Part IV: Properties of montmorillonite supported by silver chelate of hypoxanthine, Journal of Materials Science 27, 5027-5030.
- Rutherford, D.W.; C.Y.Chiou and D.D. Eberl(1997): Effect of exchange cations on the microporosity of montmorillonite. Clays and Clay minerals, 45, p534-543.
- Shalini Chaturvedi A., Pragnesh N., Dave A., Shah N. K., (2012): Applications of nano- catalyst in new era. Journal of Saudi Chemical Society, 16(3), pp 307–325.
- Vishnu Prabhakar and Tahira Bibi (2013): Nanotechnology, Future Tools for Water Remediation. International Journal of Emerging Technology and Advanced Engineering Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 3, Issue 7, July 2013) 54.
- Xiu, Z.M., Ma, J., Alvarez, P.J.J., (2011): Differential effect of common ligands and molecular oxygen on antimicrobial activity of silver nanoparticles versus silver ions. Environmental Science and Technology 45 (20), 9003 to 9008.
- Xiu, Z.M., Zhang, Q.B., Puppala, H.L., Colvin, V.L., Alvarez, J.J.P., (2012): Negligible particle-specific antibacterial activity of silver nanoparticles. Nano Letters 12 (8), 4271to 4275.
- Zhang, S.,(2006): Removal of nickel ions from wastewater by Mg(OH)₂/MgO nanostructures embedded in Al₂O₃ membranes. Journal of Alloys and Compounds. 426: p. 281-285, 2006.
- Zhou Y., Xia M., Ye Y., Hu C.,(2004): Antimicrobial ability of Cu2+-montmorillonite, Appl. Clay Sci. 27, 215-218.