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Pharmaceutical Industry Wastewater Treatment Using Organic Surfactant Modified Clay

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ABSTRACT

This study was carried out to find out how effective and efficient clay, modified with hexadecyltrimethylammonuim (HDTMA) can be as adsorbent, to reduced various contaminants in wastewater. Waste-water was collected from pharmaceutical industry using composite sampling. The result of both untreated and treated wastewater recorded. These were converted to percentage reduction. The results show percentage reduction of color (88.12%), total solid (61.60%), COD (87.47%), BOD (79.59%) and TKN (70.89%). While phenol, THC and level of heavy metals reduced to below detectable level (BDL). Hence, surfactant modified clay can serve as effective and efficient adsorbent to sorb both organic and inorganic contaminants from wastewater and act as vital material in environment treatment processes.
Keywords: Modified, hexadecyltrimethylaammonium bromide, surfactant adsorbent, contaminant

INTRODUCTION

The increase in urbanization due to use in population couple with rise in waste generated, leading to increase in wastewater. With the current emphasis in environmental health and water pollution issues, there is increasing awareness of the need to dispose of these wastewater safety and beneficially.

In recent years, there has been considerable interest in the use of low-cost sorbents, thus, a search for cheaper adsorbent material such as clay to remove both inorganic and organic contaminants from waster and wastewater. Yuh-Shan Ho and Ofomaja (2004) gave the idea of how biosorbents have been used to treat water and waste water.

Raw clay materials are negatively charge but with a lot of cations like Na^+, K^+, Ca^{++}, Mg^{++} etc on the surface; which can be ion exchanged. Ion exchange with organic cation has been used to modify the surface properties of clay materials and other natural materials. Such modified clay materials have been used to adsorb inorganic and organic contaminants. Clay minerals, modified with quaternary amine, can substantially enhance the removal of non-ionic and ionic pollutants from aqueous solution. The adsorption of cation surfactants on clay materials, and the potential application of such modified clays as environmental remediation material have been studied (Krishna *et al.,* 2001). Alkyl ammonium-modified clay materials are frequently studied because of the unique adsorptive properties of the modified materials. In order to adsorb anions, the modified surface must either possess positively charged exchange sites or there should be replacement of weakly held counter ions of the surfactants by more strongly held adsorbate counter ions. Some selective cationic surfactants provide such a modified surface for anions. Such organic modification alters the nature of clay from hydrophilic to hydrophobic when the exchange inorganic cations are replaced by surfactants like quaternary ammonium cation in the form of $[(CH_3)\ 3NR]^+$ or $[(CH_3)_2NRR^1]^+$. This replacement results in organophilic clays (Masomeh *et al,* 2010). The entire structure of clays becomes non-ionic surfactant with a solid base. The organoclays tend to swell somewhat in water, since, clays make up the bulk of the organoclay materials as natural cation exchange resin, they retain some cation exchange capacity, which help in reducing the heavy metal content of water wastewater which passes through the barrier (Alther, 2004).

In this study, $HDTMA^+$/montmorillonite organoclay materials were prepared and investigated using XRD, FT-IR and used to treat water/wastewater from pharmaceutical industry using batch treatment method.

MATERIAL AND METHODS

The waste-water samples used was obtained from a pharmaceutical factory located in Benin-City, Nigeria. The factory is a large one, as it produces various drugs both in tablets and syrup, ranging from anti-malaria drugs to anti-biotic, alongside other types of drugs.

The wastewater flow chart of the pharmaceutical industry is shown in figure 1 below.

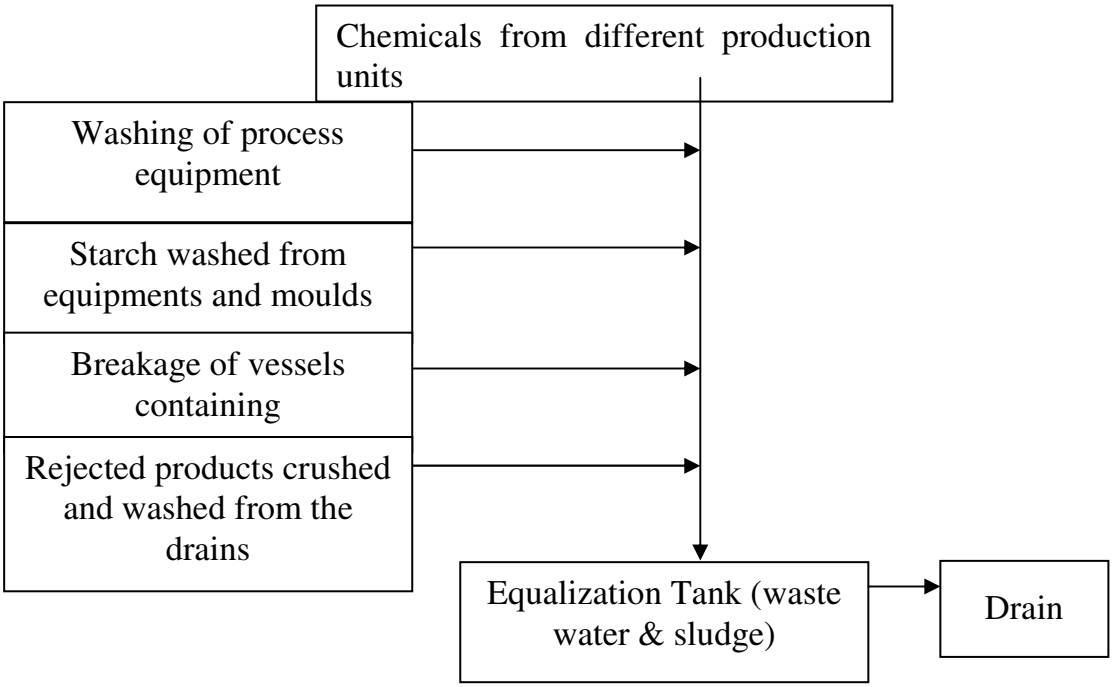


Figure 1: Waste water flowchart of a pharmaceutical industry (Source, Asia, 2011)

Clay materials used were collected from northern part of Edo State, Nigeria and pre-treated by method describe by Alther (2004).

Composite sampling was carried out by collecting wastewater samples from a particular place on hourly basis for five days for six hours to avoid unpredictable changes and preserved. The waste water samples were analyzed according to the standard methods for examination of water and wastewater (APHA, 2005) and standard methods for water and effluent analysis (Ademoroti, 1996). Ditto for the hexadecyttrimethylammonium (HDSTMA) clay materials treated wastewater.

Parameters like total solid, electrical conductivity, turbidity, colour, nitrogen (Nitrate, nitrite and ammonia), oxygen demand (COD and BOD), dissolved oxygen phenol and total hydrocarbon counts were analyzed according to the standard methods for the examination of waste and wastewater (APHA, 2005). The heavy metals content of the wastewater were determined using the atomic absorption spectrophotometric (AAS) method as described by APHA (2004) and also same for after treatment with HDTMA-modified clay materials.

Preparation of modified clay

The synthesis of the HDMA modified clay materials were performed by the following procedure – 5g of the raw clay was first dispersed in acetone, in 200ml of deionized water then left under mechanical stirrer for 5 hours. A predissolved amount of HDTMA solution was added to the clay suspension at 50^0C. Acetone was used to make the suspensions less sticky and easier to handle. Concentrations of $HDTMA^+$ used were 0.5, 1.0, 1.5, 2.0 and 2.5 CEC of the raw clay respectively. The reaction mixtures were stirred for 2 hours at this temperature. The modified clay materials were washed with deionized water repeatedly until free of bromide ions as indicated by $AgNo_3$ test. After drying at room temperature, they were ground and sieve through a 100 mesh and stored in vacuum desiccator for 5 days.

Characterization

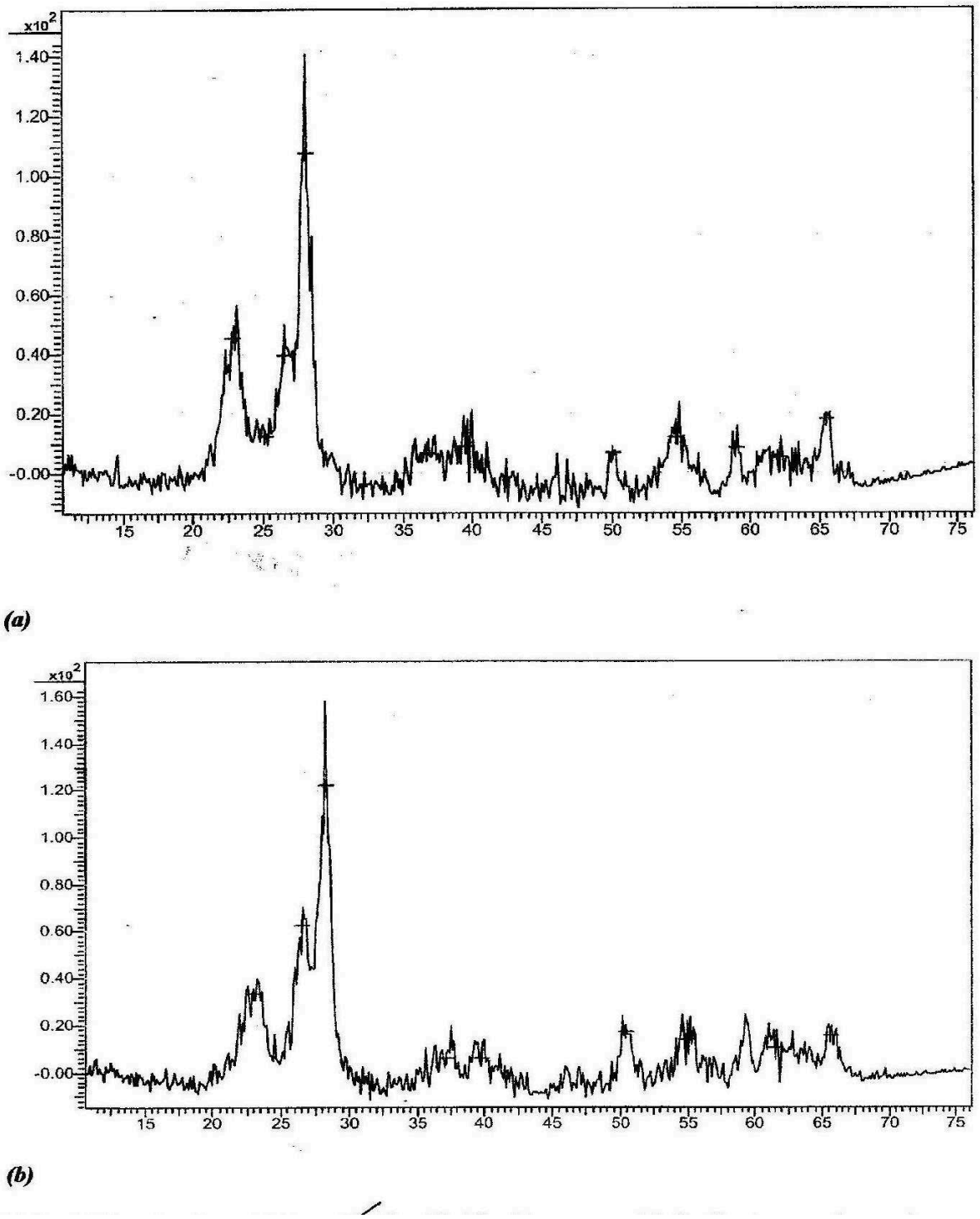
Basal spacing of the HDTMA-clay and raw clay materials were analyzed by X-ray diffraction (XRD). XRD patterns were recorded using Rigaku Rint (2000). X-ray, powder deffractometer with Cu, Ka radiation (30mA, 40Kv) from 2^0 to 10^0, in steps of 0.02^0.

Fourier transformed infrared spectroscopy (FT-IR) was performed by the KBr method with Phillip Harries, 2005 Fi-IR spectrophotometer.

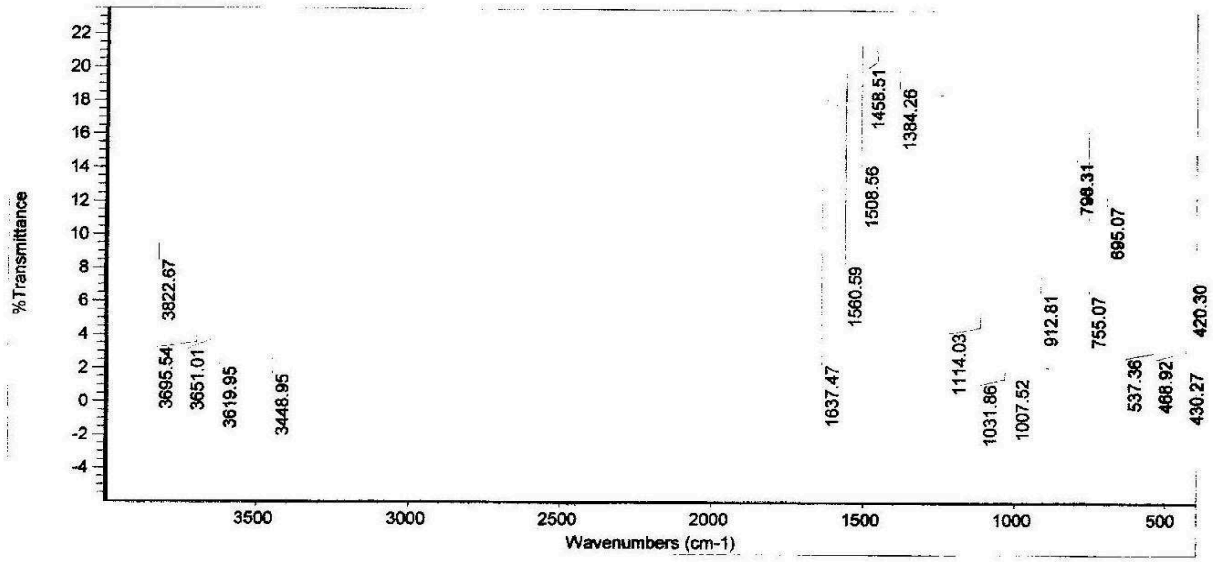
The raw clay materials used for this study were collected from clay deposit in northern part of Edo State, Nigeria. With percentage compositions 72.29% SiO_2, 7.80%, Al_2O_3, 15.04%, Fe_2O_3, 0.20%MgO, 2.80% CaO, 1.01%, Na_2O, 1.94% K_2O, 4.03% MnO, 13.14 structural water (H_2O) and 5.01 pH. Cation exchange capacity CEC, 92.13 meq/100g and surface area of 26.36m^2/g.

RESULTS AND DISCUSSION

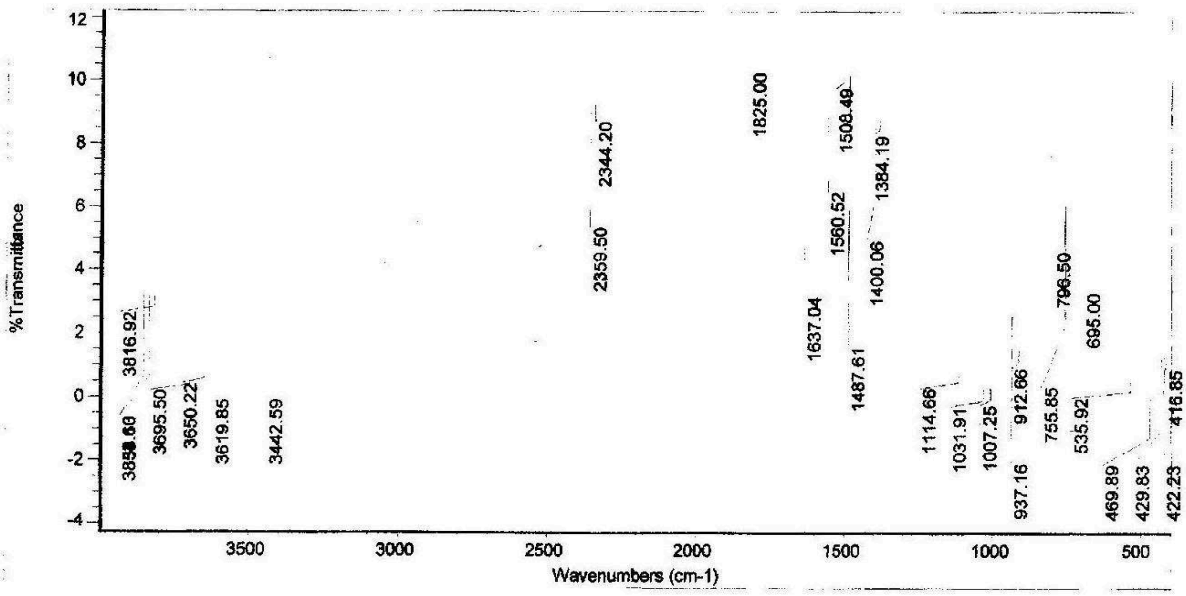
Results of the X-ray diffraction analysis are modified and unmodified clay materials are shown in Fig. 1.



X-Ray Diffraction Data (a) Raw Clay (b) After Treatment with the Quaternary Ammonium Salt



(a)



(b)

Infrared Curves of (a) Raw Clay (b) After Treatment with the Quaternary Ammonium Salt

Table 1: Result of raw and treated pharmaceutical industry wastewater using HDTMA modified clay.

	Untreated wastewater	**Treated waste water**
pH	4.90 ± 20	7.07 ± 0.00
Turbidity (NTU)	16.17 ± 0.32	3.02 ± 0.17
Ec (µs/cm)	889,27 ± 0.64	400 ± 0.00
Color (pt.co)	10.10 ± 0.30	1.20 ± 0.00
TS (mg/l)	67.97 ± 0.25	26.10 ± 0.90
DO (mg/L)	1.20 ± 0.20	4.17 ± 0.29
COD (mg/L)	399.13 ± 1.82	50.03 ± 0.05
BOD (mg/L)	147.12 ± 1.13	30.02 ± 0.06
NH_4^+N(mg/l_	3.87 ± 1.41	BDL
NO_3^-N(mg/l)	2.22 ± 0.60	0.90 ± 0.01
TKN (mg/l)	6.87 ± 0.23	2.00 ± 0.01
Oil and grease (mg/l)	5.09 ± 0.01	BDL
Phenol (mg/l)	5.55 ± 1.18	BDL
THC (mg/l)	3.57 ± 0.37	BDL
Cd (mg/l)	0.03 ± 0.00	BDL
Cu (mg/l)	0.02 ± 0.00	BDL
Zn (mg/l)	0.09 ± 0.00	BDL
Cr (mg/l)	0.016 ± 0.001	BDL

BDL = Below Detectable level
DO = Dissolved Oxygen
BOD=Biochemical Oxygen Demand
THC = Total Hydrocarbon count
TS = Total Solids
COD=Chemical Oxygen Demand
EC = Electrical Conductivity
TKN = Total Kjedalh Nitrogen

Table 2: Percentage reduction after treatment of wastewater with HDTMA modified clay

Parameters	**% Reduction**
1. Color	88.12
2. TD	61.60
3. COD	87.47
4. BOD	79.59
5. TKN	70.89

ASSESSMENT OF TREATMENT EFFICIENCY

From the results as shown in table 1, the pH became slightly alkaline, as the color changed to colourless. HDTMA modified clay materials reduced electrical conductivity and total solids. This can be attributed to its high cation exchange capacity and surface area. The results of the COD and BOD reduction depicted in table 2 show that considerable reductions were achieved with HDTMA – clay. This can be attributed to dispersion of contaminants in the wastewater into the clay interface layer as the clay is bound to swell less as its cohesive forces can keep the molecules together. This can range from strong valence bonds to weaker Van Der Waals forces of attraction (Alther, 2004, Mesomeh *et al* 2010, Egbon 2011). In order to adsorb anions, the modified surface must either posses positively charged exchange sites or there should be replacement of weakly

held counter ions of the surfactant by more strongly held adsorbate counter ions. This invariably enhance adsorption of contaminants (Krishna, et al 2001).

The result fo percentage reduction of nitrogen reduction by HDTM-clay was impressive. The chemical state of the nitrogen (NH_4^+ Nm NO_3^-N, TKN) in the wastewater determines how much of it is abstracted from the wastewater. Any of these forms of nitrogen can be absorbed on the HDTMA – clay surface or replaced by ion exchange. The removal efficiency of organoclay for oil and grease, phenolic compounds can be attributed to partitioning. That is, raw clay (hydrophilic) now HDTMA clay (hydrophobic), becomes non-ionic surfactant with a solid base. As organic compounds pass by the particles, they dissolve into the organic phase, where they are more soluble and these bind on the clay surface and easily released safely back into the environment as fertilizer (Alther, 2004).

Since there are always more amine chains available than be stiochiometrically affixed to the montmorillonite; the reminder tends to adhere to the fixated surfactant chain by a tail-tail interaction. That means that a non-ionic HDTMA-clay materials have small positive charge, which allows it to remove some anions. Since clays makes up the bulk of the organoclay, it invariably acts as a natural exchange resin; it retains some cation exchange capacity, which helps in reducing the heavy metal content to below detectable level. Thus, the hydrophilic end removes water soluble contaminants while organophilic end helps remove organic base contaminants like phenolic compounds and oil and grease present in pharmaceutical wastewater.

CONCLUSION

In conclusion, the results revealed that pollutants from wastewater can be reduced by using HDTMA-clay materials either through ion exchange (or CEC) or adsorption mechanism; as the raw clay change from hydrophilic to hydrophobic, these two properties enhance the adsorbtion capacity efficiency of $HDTMA^+$ – clay materials in water and wastewater treatment processes. Thus, surface modification of montmorillonite clays by surfactant like $HDTM^+$ offers an easy method of adsorbing large amounts of contaminants (inorganic and organic) from water and wastewater from the environment.

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