Adsorption of Acetaminophen from aqueous solutions onto hexadecyltrimethylammonium modified kaolinite

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Abstract: In this study, N-acetyl-p-aminophenol (APAP) otherwise known as acetaminophen, a pharmaceutical active compound, was adsorbed from aqueous solution onto cetyltrimethylammonium bromide (CTAB) (hexadecyltrimethylammonium) functionalized kaolinite clay (CTAB–Kao). The modification of CTAB–Kao was corroborated by the use of the Fourier transformed infrared (FTIR) spectroscopy technique. The effect of varied pH, adsorbent dose, initial adsorbate concentration and contact time on the adsorption capacity of CTAB-Kao was investigated by batch adsorption process and compared with that of unmodified kaolinite clay (kao). The moderately basic nature of CTAB-Kao deprotonated the Phenolic end of APAP producing nucleophilic phenoxide anion or phenolate ion, that instigated repulsion between APAP and CTAB-Kao. The resultant of this nucleophilicity between both adsorbent and adsorbate brought about insignificant APAP removal from aqueous solution. When compared with Kao that has a negatively charged edge, the removal of APAP was not significantly attainable because of the same phenomenon.

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1. Introduction

The most essential environmental issues of our time is protecting the integrity of our water resources. Potential adverse human and ecological health effects resulting from the production, use, and disposal of numerous chemicals that offer improvements in industry, agriculture, medical treatment and even common household conveniences calls for a serious concern (Zhou et al., 2006). Pharmaceuticals, as well as biogenic hormonal wastes are released directly to the environment even after passing through wastewater treatment processes (even domestic septic systems), which often are not designed to remove them from the effluent (Robinson et al., 2007). The occurrence and fate of pollutants especially pharmaceutically active compounds (PhACs) in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry (Stan and Heberer, 1997; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Daughton and Jones-Lepp, 2001; Ku¨mmerer,2001; Verstraeten et al., 2000).

In addition, several investigations have also shown some evidences that substances of pharmaceutical waste origin are often not biodegraded in the environment (Ternes, 1998; Daughton and Ternes, 1999; Zwiener et al., 2000;). Therefore it is very expedient to remediate it before it spread through the streams, arteries of rivers and others as well as diffusing into groundwater. The possible sources and pathways for the occurrence of pharmaceutical residues in the aquatic environment are through agriculture application of large amounts of veterinary drugs and feed additives in livestock breeding, landfill leachates of pharmaceutical residues in the environment (Eckel et al., 1993; Holm et al., 1995; Ahel and Jelicic, 2001) or manufacturing byproduct residues as shown by schematic pathway illustrated by Thomas Heberer (2002) (**Figure 1**). Acetaminophen (**Figure 2**) is one of the pharmaceutical active ingredients for the production of paracetamol, a widely used in analgesic drugs formulation, both in the single-ingredient and multi-component ones. It is accepted as a very effective treatment for the relief of pain and fever in a variety of patients including children, pregnant women, and the elderly (Ward and Alexander1999). There are several methods for the removal of pharmaceutical organic pollutants; some of which are membrane process, ion exchange, biological degradation, and adsorption process using various kind of adsorbents (Ince and Apikyan 2000; Srivastava et al., 2005; Yavuz and Koparal 2006; Vazquez et al., 2006). Adsorption process is proven to be an effective process because it is capable of removing pollutant in wide range of concentrations (Kumar 2007). Adsorption processes involve the mass transfer of adsorbate molecules from aqueous medium toward active sites on an adsorbent either by external and intraparticle diffusion or on the active sites in the pores surfaces (Kumar 2007). Adsorption process using activated carbon is the most popular technique for organic contaminants removal due to its efficiency. It removes organic contaminants from wastewater, either by adsorption or by combination of adsorption

and ion exchange. However, due to high operational and regeneration cost, researchers has sought for alternative and consequently, numerous low-cost alternative adsorbents have been proposed. These includes low cost agricultural wastes such as chemically modified sugarcane bagasse lignin (Da Silva et al., 2011), Pistachio hull waste (Moussavi and Khosravi, 2011), Coffee husk-based activated carbon (Ahmad and Rahman, 2011), Pine cone (Mahmoodi et al., 2011), Rice husk (Safa and Bhatti, 2011), peat (Ramakrishna and Viraraghavan 1997), pine sawdust (Ozacar and Sengil 2005), Synthetic calcium phosphates (Boujaady et al., 2011) and clay minerals such as; natural untreated clay (Errais et al., 2011), Kaolinite (Xue-Song et al. 2006), sepiolite (Eren and Afsin 2007), mont-morillonite, Bentonite and nanocomposites (Wang and Wang, 2007). The applications related to the sorption properties of kaolinite clay have been developed, unfortunately the sorption capacity of natural kaolinite is limited for organics because of its significantly low specific surface area (SSA) and hydrophilicity induced by the exchangeable metal cations on the clay, which has resulted in its ineffectiveness in the adsorption of organic compounds. Therefore, to improve the adsorption capacity of these adsorbent, surface modification has been conducted and investigated (Srinivasan and Fogler 1990; Favre and Lagaly 1991; Breakwell et al., 1995; Bergaya and Lagaly 2001; Martens et al., 2002; Xi et al., 2005; Filho and Carmo 2006; Rugmini and Menon 2008; Yahaya et al., 2009; Yahaya et al., 2012). Quaternary ammonium cations of the general form $(CH_3)_3\ NR)^+$ or $(CH_3)_2NR_2^+$ were used as exchange ions on clay and the uptake of organic analytes from water was studied. It was shown that quaternary ammonium cations with relatively large R groups, such as hexadecyltrimethylammonium ($R = [CH_3–(CH_2)_{15}–N(CH_3)_3]^+$) is more effective (Lee, 1990). This process of modification is referred to as organo-clay. Modification changes the nature of the surface of an organoclay from hydrophilic to hydrophobic or organophilic by being organofunctionalized. ((Srinivasan and Fogler 1990). This process alters the structure, chemical composition, and physical properties of the kaolinite clay, at the time enhancing its adsorption capacity (Gil et al., 2011). The objective of this study is to investigate the adsorption potential of hexadecyltrimethylammonium modified kaolinite at the removal of spiked N-acetyl-p-aminophenol (APAP) otherwise known as acetaminophen from aqueous solution relative to unmodified kaolinite clay.

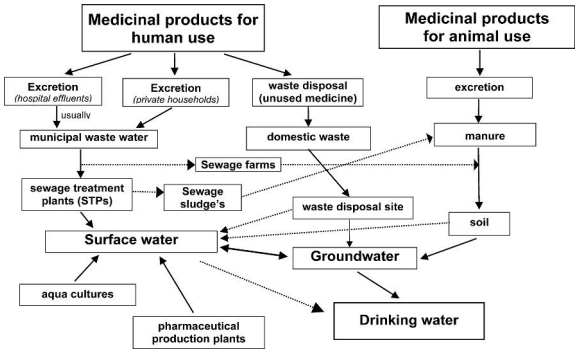

Figure 1. Scheme showing possible sources and pathways for the occurrence of pharmaceutical residues in the aquatic environment.

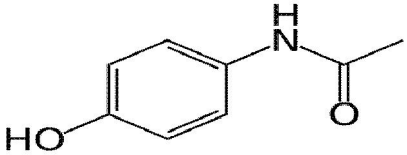

Figure 2. N-acetyl-p-aminophenol (APAP) otherwise known as acetaminophen

2.0 Materials and Methods

2.1 Adsorbate and modifier

Acetaminophen referred to as APAP in this study was obtained from Aldrich Chemical Company (99 % purity) and used as obtained without further purification (Fig. 1). hexadecyltrimethylammonium also known as Cetyltrimethylammonium bromide (CTAB) a white powder quaternary amine cationic surfactant, used for clay modification was supplied by Aldrich Chemical (Sigma–Aldrich Chemie GmbH, Germany). The molecular information of acetaminophen is shown in **Table 1**. Other chemical reagents used in this study were of high purity.

Table 1 Molecular properties of acetaminophen (APAP) and cetyltrimethylammonium bromide (CTAB)

Properties	APAP	CTAB
C/ formula	$C_8H_9NO_2$	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
M/Wt	151.163 g/mol	364.45 g/mol
Solubility	1.236 g/cm^3 (20^{0}C)	1 mmol/L (25^{0}C)
Density	12.78 g/L	-
Melting Pt	169 ^{O}C.	237 -243 ^{O}C
λmax (UV)	245nm	-

2.2. Adsorbent preparation and modification

Kaolinite Clay was obtained from Ubulu-Ukwu in Delta State, Nigeria. Stones and other non-clay particles were removed from the sample by hand picking. It was then crushed and sieved through a meshed sieve to further remove the larger non-clay fractions. 100 g of the clay sample was dispersed in

distilled deionized water and stirred continuously with a stirrer for 6 h. Two layers were formed - a settlable heavier particulate layer and a colloidal suspension which is the kaolinite clay. The suspended layer was carefully and completely decanted after which the colloidal layer is recovered by centrifugation. It was further purified by using Renolds and Moores (1989) method**.** This involves the addition of 30 % hydrogen peroxide to the sample solution solution and continuously stirs till all effervescence has ceased. The mixture was then kept standing overnight to allow any carbonaceous substance to be oxidized and with this treatment any organic substances remaining in the clay is removed. The supernatant was decanted and the Kaolinite clay washed thoroughly with distilled-deionized water to remove traces of hydrogen peroxide. The peroxide free Kaolinite clay was recovered and oven dried at 353 K to obtain the natural and unmodified kaolinite clay sample (Kao). The dried sample was carefully crushed and sieved to produce the desired particle size. 50 g of Kao was treated with 1 mol/L NaCl solution to saturate the cation exchangeable sites on the adsorbent with sodium ions. The solution was stirred continuously to allow a complete reaction, after which the sodium-kaolinite (Na-Kao) clay formed was washed free of chloride by testing for the presence of chloride using $AgNO_3$.

2.3. Preparation of CTAB-kaolinite

10 g of Na-Kao was dispersed in 0.2 L of distilled deionized water at an ambient temperature, stirred and allowed to solubilize for 2 h. CTAB was dissolved in a separate container at a solution concentration of 0.03 mol/L and slowly it was added to the dispersed Na-Kao. The reaction mixture was slowly stirred by mechanical stirrer at a temperature of 50 ^{0}C in a thermostated water bath for 24h. Then the product, organo-kaolinite (CTAB-Kao) was washed free of bromide anion (tested with $AgNO_3$), dried in an oven at 80 ^{0}C and carefully ground to powder before use.

The characterization of CTAB-Koa modified and Koa unmodified clay surface functionality was determined by SHIMADZU Fourier Transform Infrared spectrometer (FTIR).

2.4. Adsorption study

A stock solution of 1000 mgl^{-1} acetaminophen was prepared. Various concentrations of APAP were prepared from the stock solution and were read on a UV–vis spectrophotometer [surgifriend SM7504UV/visible 911]. A calibration curve of absorbance against APAP concentrations was obtained by using APAP solutions of known concentrations (in the range of 10–400 mgL^{-1}) from which a linear curve with a high correlation coefficient (R^2 = 0.9931). The correlation coefficient of the calibration curve in the present study allows us to consider the molar absorptivity constant applicable over the range of concentration investigated. Thus, the APAP concentration will be determined with good precision. The adsorption experiments were all carried out using amber bottles so as to reduce the intensity of light reaching the solution. The following conditions were maintained for different adsorption study experiments:

Effects of pH	Adsorbents 0.08 g; APAP -10 mg/l; temperature 304 K; interaction time 360 min; pH 2.0–10.0 at unit intervals
Mass Variation	`Adsorbent doses 0.025-1.25g; APAP 50 mg/l; interaction time 360 min; pH = 6.80 at ambient temperature
Concentration Variation	Adsorbent 0.5 g; APAP 10 - 100 mg/l; interaction time 360 min; pH =6.80 at ambient temperature
Kinetics	Adsorbents 2.5 g; APAP 50 mg/l; interaction time 30 sec -360 min at ten different intervals; pH 6.80 at ambient temperature;
Isotherms	Adsorbent 0.5 g; APAP 10 - 100 mg/l; interaction time 360 min; pH 6.80 at ambient temperature.

In order to obtain the value of the adsorption capacity, the amount of APAP adsorbed (q_e) onto organokaolinite (CTAB-Kao) and the unmodified (Kao) were evaluated using the following expression:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

$$\%removal = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where V (l) is the volume of APAP solution; Co (mg/l) and Ce (mg/l) are the initial and equilibrium concentrations of APAP in solutions and m (g) is the mass of adsorbents.

2.5 Adsorption Kinetics

Kinetic models, i.e. the pseudo-first order, the pseudo-second order and intraparticle diffusion models were considered for interpreting the experimental data obtained:

2.5.1. Pseudo-first-order model.

The pseudo-first order kinetic model of Lagergren (1898) was used in order to estimate the adsorption capacity of the adsorbent:

$$\ln(qe - qt) = \ln(qe) - k_1 t \quad (3)$$

where q_e and q_t (mgg^{-1}) are the amounts of APAP adsorbed onto the adsorbents at equilibrium and at various times t (*min.*); k_1 (min^{-1}), is the rate

constant of the pseudo first-order model for the adsorption process.

The rate constant k_1 and qe were obtained from the slope and intercept of the linear plots of ln (qe −qt) against t, respectively.

2.5.2. Pseudo-second-order model.

The pseudo-second-order reaction model (Ho and McKay 1998) is expressed as

$$\frac{t}{q_t} = \frac{1}{\left(k_2 q_e^2\right)} + \frac{t}{(q_e)} \quad (4)$$

where k_2 ($g\ mg^{-1} min^{-1}$) is the rate constant of the pseudo-second-order model for the adsorption process q_e (*mg/g*) and q_t (*mg/g*) have the same definition as above for equation (4) and were obtained from the intercept and slope of the linear plots of t/qt against t, respectively.

2.5.3 The intraparticle diffusion

The intraparticle diffusion equation was used accordingly which is written as

$$q_t = k_p t^{0.5} + I \quad (5)$$

where q_t is same as defined as above, k_p, ($mg\ g^{-1}\ min^{-0.5}$) the intraparticle diffusion rate constant and *I,* gives an idea about the thickness of the boundary layer, i.e., the larger the intercept the greater is the boundary layer effect (Mall et al., 2005). If intraparticle diffusion is the rate determining factorTo follow the intra-particle diffusion model, a plot of *qt* against $t^{0.5}$ should give a linear line where a slope is k_p and intercept *I*..

2.6. Adsorption Isotherms

2.6.1. Langmuir Isotherm

The Langmuir isotherm has been widely applied to pollutants sorption processes. A basic assumption of the Langmuir theory is that the adsorption takes place at specific homogenous sites in the adsorbent. Moreover, when a site is occupied by a solute, no further adsorption can take place at this site (Langmuir 1918). The Langmuir adsorption isotherm can be written as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (6)$$

where q_e ($mg\ g^{-1}$) is the amount of APAP adsorbed onto clay samples at equilibrium, $q_{\max}$ ($mg\ g^{-1}$) is the theoretical monolayer capacity, K_L (*l/mol*) is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption and C_e ($mg\ l^{-1}$) is the equilibrium solution concentration. The values of $q_{\max}$ and K_L are evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e respectively.

2.6.2 Equilibrium parameter

One of the essential characteristics of the Langmuir equation is that it could be expressed by dimensionless constant called equilibrium parameter (R_L). R_L is calculated using the following equation:

$$R_L = 1 \big/ \left(1 + K_L C_O\right) \quad (7)$$

where k_L ($dm^3\ mol^{-1}$) is the Langmuir constant and C_0 ($mg\ L^{-1}$) is the highest initial dye concentration. The parameter indicates the favourability of isotherm such that when irreversible

($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Sivaraj et al., 2001).

2.6.3. Freundlich isotherm

The Freundlich isotherm which is used to describe heterogeneous systems is expressed by the following empirical equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Where K_F ($L\ g^{-1}$) and n (dimensionless) are the Freundlich adsorption isotherm constants. The values of K_F and n are evaluated from the intercept and the slope of the linear plot of ln qe againt Ce respectively.

3.0. Result and Discussion

3.1. FTIR analysis

FTIR spectra of CTAB-Kao and Kao were measured within the range of 500 – 4000cm^{-1} (**Figure 3**). Kaolinite has characteristic signature of O–H stretching pattern that consists of four bands at approximately 3697, 3667, 3652, and 3620 cm^{-1}.These hydroxyl groups are aligned almost parallel to the plane, thus pointing in the direction of the unoccupied octahedral hole (Temar et al., 2008).

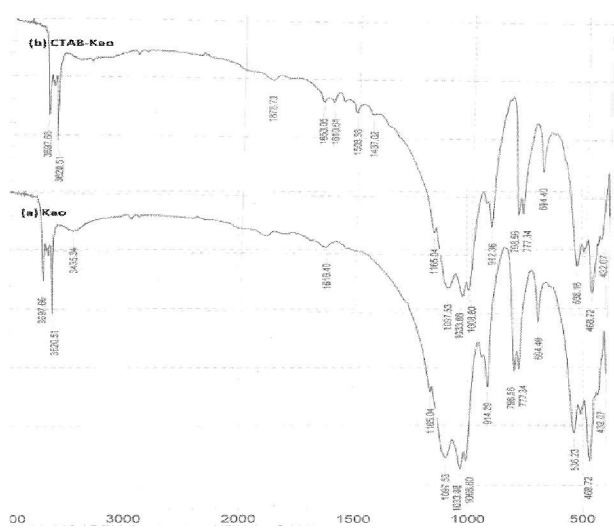

Figure 3 FT-IR spectra of (a)Kao and (b)CTAB- Kao adsorbents.

And according to Temar et al., (2008) the band at 3620 cm^{-1} is attributed to the stretching frequency of the internal (inner) hydroxyl band of kaolinite which is not usually influenced by the interlayer modification of kaolinite as shown by the FTIR spectra for CTAB-Kao and Kao (**Figure 3**). The remaining bands; 3697, and 3652 cm^{-1} (**Figure 3**) are associated with the external (outer) hydroxyl groups. The band at 3697 cm^{-1} corresponds to stretching vibrations of hydroxyl (νOH) groups attached to octahedral sheet located in the interior blocks of Kao and CTAB-kao.The peaks at 1437 and 1508 cm^{-1}**,** gave a clue of the possibility of the intercalation of CTAB molecules between the aluminosilicate layers, this band is obviously absent on the Kao spectra. The Si-O coordination bands at 1165, 1097 and around 912 and 914 $cm^{-1}$are observed as a result of the Si-O vibrations. The band at 1033 cm−1 represents the stretching of Si-O in theSi-O-Si groups of the tetrahedral sheet (Sabah and Celik 2002) The bands at 536 and 468 cm−1 are due to Si O Al (octahedral) and Si O Si bending vibrations respectively. These differences in the appearances of peaks at different bands are indication that the organo-kaolinite modification with CTAB is successful.

3.2. Effect of pH

The chemical characteristics of both adsorbate and adsorbent vary with pH. Therefore, the pH of an aqueous medium is an important factor that may influence the uptake of the adsorbate. In this study, the effect of pH were carried out in the range of 2-10 to investigate the removal of APAP by the adsorbents. The pH of the solutions was adjusted by adding (0.1M) HCl or NaOH. According to the resonance structure shown in Figure 4, the deprotonation of the phenolic edge of acetaminophen to phenoxide anion and the conjugation on the APAP molecule thus greatly reduces the basicity of the oxygen and the nitrogen (**Figure 4**), thereby making the hydroxyl acidic through delocalization of charge developed on the phenoxide anion. It was discovered that the removal of APAP by Kao was not significantly attainable by the adsorbent at both increased and decreased solution pH (**Figure 5**).

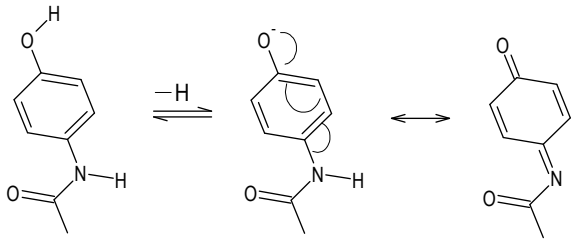

Figure 4. Resonance structure of acetaminophen phenoxide anion end.

This is possibly because at lower pH, APAP exists in a unionized form and as pH increases, it is converted into negatively charged phenolate ion and the negatively charged edge of Kao repels it.

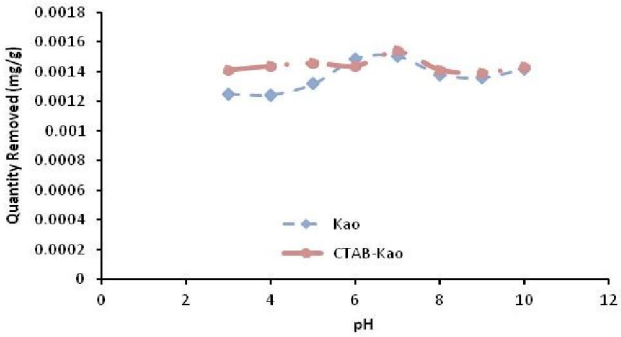

Figure 5 Effect of pH on the removal of APAP from aqueous solution onto Kao and CTAB-Kao.

Similarly the percentage APAP removed by CTAB-Kao was insignificantly low at all the pHs which also mean that the Phenolic end of APAP has been deprotonated with the moderately basic nature of trimethylamine of the organic modifier (CTAB) of organokaolinite, forming the nucleophilic phenoxide anion or phenolate ion, hence there is repulsion between APAP molecule and CTAB-Kao as a result of nucleophilicity of both adsorbent and adsorbate there is reduction in the resultant adsorbate removal.

3.3. Adsorbent dose variation

The investigation of the efficiency of an adsorption process design through adsorbent dosage variation is based on the fact that an increase in adsorbent dosage will lead to increased adsorbent surface area and availability of more adsorption sites.From fig. 5 it is obvious that the removal of APAP by both Kao and CTAB adsorbents from aqueous solution was insignificantly and almost impossible as it is in microgram. This may however be due to the repulsion that exist between the adsorbate and the adsorbents. The minimal quantity of APAP removed that was observed (**Figure 6**) is based on physiosorption attributed to mass transfer of APAP into the pores and interlayer spaces the existed in the adsorbents and possible van der waal molecule attraction to the adsorbents as the masses of the adsorbents were increased.

3.4. Adsorbate concentration variation

The influence of the initial concentration of APAP in the solutions on the rate of removal onto CTAB-Kao and Kao adsorbents were investigated at various concentrations. From Figure 7, when the initial APAP concentration was increased from 10 – 100 mg/l, the adsorption was not feasible but given a negative UV adsorbance which is an indication that no

APAP was adsorbed by the adsorbents. However at higher APAP concentration there is some quantities of APAP removal recorded (**Figure 7**) which may have resulted from overwhelming of the adsorbent surface repulsion by extra concentration influx of APAP. Otherwise the rate of adsorption is very insignificant with increase in initial APAP concentration as a result of none driving force of attraction between the adsorbent and adsorbate in solution.

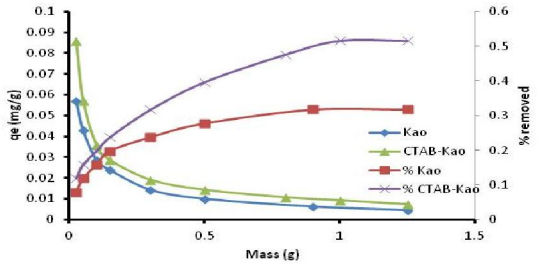

Figure 6. Adsorbent dose variation for the removal of APAP from aqueous solution onto Kao and CTAB-Kao.

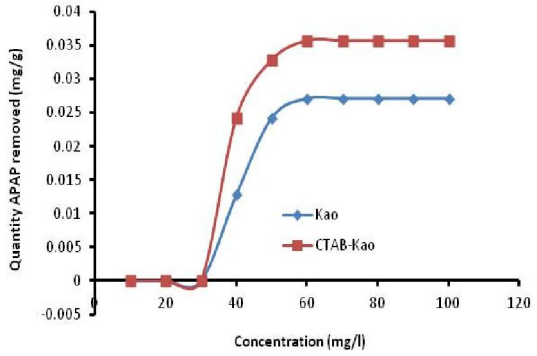

Figure 7 Adsorbent dose variation for the removal of APAP from aqueous solution onto Kao and CTAB-Kao.

3.5. Contact Time and kinetics

The adsorption of APAP onto KAO and CTAB adsorbents was studied as a function of contact time in order to decide the attainability of equilibrium with time. In this study, an adsorbent constant mass of 25.0 g/L was dispersed and agitated in 500ml of 100, 150 and 300mg/L adsorbate solutions concentration at pH = 6.80 using a three impeller mechanical stirrer. The samples were taken at ten different time interval that spanned over a period of six hours (**figure not shown**). After the adsorption reaction process it was observed that the adsorption equilibrium was not determinable at a lower concentrations (ie 100 and 150 mg/l) because from the observed experimental data at these concentrations, even at a higher adsorbents masses it is obvious that there was no adsorbent-adsorbate interaction at all between APAP and the adsorbents. However at 300 mg/l the quantity adsorbed were infinitesimal and erratic (Fig. 8). Evidentially, it can be inferred that there is an occurrence of adsorbate-adsorbent repulsion occurred in the presence of APAP solution interacting with a large quantity of negatively charged adsorption sites of Kao and slightly basic CTAB –Kao adsorbents adsorption surfaces. The high APAP concentration and large adsorbent dose which was meant to enhance their interaction since there was no interaction at lower APAP concentrations instead the adsorbents tend to repel APAP thereby hindering interaction. However, there was a kind of van der waal attraction at a given time and at another time it will be broken off and repulsed as the reaction agitation continued. It will be erroneous to apply the data obtained thus far in the determination equilibrium capacity of the adsorbents and in the determination the order of reaction through the adsorption kinetic study.

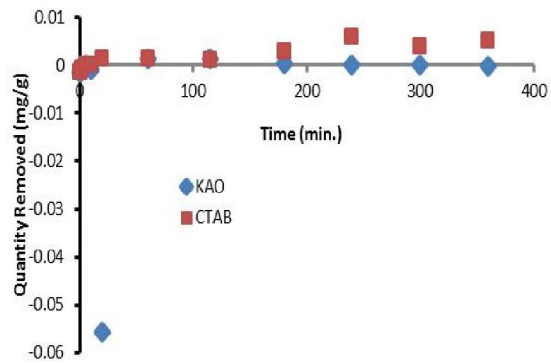

Figure 7. Contact time for the removal of APAP from aqueous solution onto Kao and CTAB-Kao.

3.0. Conclusions

In this study, the adsorption characteristics of CTAB-Kao followed a similar pattern as the unmodified kaolinite clay sample because of none interaction between APAP and the adsorbents. However the minimal removal of APAP observed is obviously due to physiosorption driven or van der waal attraction after a long time of adsorption interaction. This study shows that APAP cannot effectively be removed from the aqueous medium by the use of neither unmodified nor trialkyl-ammonium modified kaolinite clay.

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