

Adoption of Response Surface Methodology in the Optimization of Ammonia Removal from Aquaculture Effluent Using Thermal Activated and Non-Activated Ball Clay

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Abstract

This study evaluates the adsorptive removal of ammonia from aquaculture effluent by Thermally Activated Ball Clay (TABC) and Non-Activated Ball Clay (NABC) adsorbents. Experimental design and number of experimental runs was executed by Response Surface Methodology (RSM) "Design Expert version 13". Characterization of TABC and NABC by Scanning electron microscope (SEM) and Fourier transformed infrared spectroscopy (FTIR) revealed the presence of porous morphology and functional groups: hydroxyl, carboxylic, hydrogen bonding and aldehyde group that aids ammonia adsorption. Effect of varying pH, temperature, dosage and contact time on ammonia removal were carried out within the pH (3-11), temperature (298 – 318K), time (30-90 minutes) and adsorbent dosage (0.5 - 2.5 g) in 100 mL of solution. At equilibrium, the amount of ammonia removed from the aquaculture effluent and the removal efficiency range from 3.39mg/mL (92.87%) to 3.60 mg/mL (98.63%) while from 0.05 mg/mL (1.369%) to 3.59 mg/mL (98.35%) for NABC with the corresponding adsorption capacities TABC (0.678 – 0.720) and NABC (0.0018 – 0.718) respectively. The adsorptive removal mechanism was best explained by the Blanchard pseudo-second order kinetic model and Langmuir adsorption isotherms. The adsorption of ammonia on TABC was better than NABC. Further study is suggested on other modifications of ball clay.

Keywords: Ammonia, adsorptive removal, optimization, ball clay and RSM

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I. Introduction

Aquaculture is a sustainable practice of fish production which provides an alternative to wild fish sanctuaries throughout the world. It is a systemic rearing of fish in a confined water body such as tanks and ponds, where its development can be monitored and controlled (Adewumi, 2015; Sodeinde *et al.*, 2022).

The practice have played an important role in the development of many nations economy as well as enhances the socioeconomic resilience of rural areas, potentially offering valuable and skill-based employment opportunities and in some cases, stabilizing the economic base of many communities (Haylor and Bland, 2013).

Fish production is very important for since fish is one of the most staple food items and valuable source of protein for man. However, many aquaculture systems generate high amounts of wastewater containing compounds such as suspended solids, total phosphorus and nitrogen compounds such as ammonia capable of infiltrating into other water bodies (Yerima *et al.*, 2022a). Today, aquaculture is imperative because fish demand is on the increase likewise the amount of waste generated is directly proportional to the fish production. As these wastes increases, the concentration of organic matter, nutrients and suspended solids in water also increases thereby decreasing oxygen levels in water, while increasing chances of eutrophication, and turbidity in receiving waters (Lin and Yi, 2013; Yerima *et al.*, 2022b).

To curb these menaces, so far, a number of physical, chemical and biological methods have been employed in conventional wastewater treatment as well as in aquaculture systems. Chemical method may

involve the use of biochar as adsorbent or special clay such as clinoptilolite, bentonite, zeolite and smectite (Sodeindeet *et al.*, 2022).

The aim of this study is to optimize adsorptive removal of ammonia (NH_3) from aquaculture effluent by means of Response Surface Methodology (RSM) using Ball clay as adsorbent usually consisting of 20-80% kaolinite, 10-25% mica, 6-65% quartz, as well as trace amount of organic matter in its composition.

Response surface methodology (RSM) is a robust method that deduces an empirical model which fit the experimental data by comparing statistical variables with the sole aim of optimizing the adsorption process to make sure that the maximum adsorbent surface has been utilized in the reaction by the pollutant molecules. By this, the minimum cost of the process could be anticipated during scale-up (Sasidharan and Kumar, 2022).

One of the major component of aquaculture waste is ammonia; a toxic compound that can adversely affect fish health depending on its chemical form, pH and temperature of the water. The unionized form (NH_3^0) does migrate from water into fish, and once inside, some converts to the ionized form (NH_4^+), which then causes cellular damage (Stuart and Levit, 2010).

Ammonia toxicity in water bodies is a global problem. Ammonia in water come from fish excreta, fish feed and the protein rate in the feed been used. As the feed's protein is broken down in the fish's body, some of the nitrogen is used to form a protein (muscle), energy, and excreted through the gills as ammonia. For every ton of fish production, aquaculture operation, produce between 42 and 66kg of nitrogen waste. It principally comes from protein degradation and is present either as ionized (NH_4^+) or unionized (NH_3) ammonia (Mandakiniet *et al.*, 2021).

II. Materials and Methods

Experimental Runs Determination

The number of experimental runs to be carried out in order to obtain the optimum adsorptive condition for ammonia was determine by the aid of "Design Expert version 13" software at varying temperature (25-45°C), varying dosage of ball clay adsorbent (0.5g-5g), varying pH (3-11) and varying contact time (30-90 min).

Sample Collection

The Ball clay used as adsorbent in this study was obtained from Central drug house (P) Ltd. 7/28 Vardaan, Daryaganj, New Delhi-110002 (INDIA) and was identified by the Department of Soil Science, Federal University Wukari, Taraba State.

The aquaculture effluents were collected by stratified sampling technique using a pre-cleaned plastic container in fish ponds located at Pwadzu, Ando-moto, New site and Federal university communities of Wukari, Nigeria respectively. The water samples were homogenized to obtain a composite water sample and its ammonium content determined before adsorptive removal of ammonium (Yerima *et al.*, 2020).

Sample Preparations and Conditioning

Ball clay (166.62g) was calcined in a muffle furnace at 600°C for 1 hr. It was then cooled, sealed in an air tight container and labeled as TABC for future use. Varying amounts of thermally activated ball clay (0.5 - 5g) as proscribed by the design expert software were weighed into 25 different sets of 100mL aquaculture effluent composite samples. Drop-wise addition of 0.1 M NaOH and 0.1 M HCl were used to adjust the pH of the solution with the aid of a pH meter until the desired pH (Range from 3-11 as proscribed by design expert) was obtained. The solutions were stirred at varying time (30-90mins) and varying temperature (25-45°C) (as proscribed by design expert software) with the aid of mechanical shaker and a water bath respectively until equilibrium was achieved. The equilibrium mixture was filtered with a filter paper to obtain a clear filtrate for onward determination of residual ammonium concentration while the ammonium content of the composite sample was noted before treatment. The same procedure was carried out for Non-Activated Ball Clay (NABC).

Characterization of Ball Clay

The Scanning Electronic Microscope (Model JOEL JSM 7600F) operated with an argon atmosphere using a current of 6 mA for 3 min was used to examine the morphology of TABC and NABC. While the functional groups were determine by the Fourier transform infrared spectroscopy (FT-IR) (Model Nicolet iS10 FT-IR Spectrometer) with all spectra were recorded from 4000 to 400 cm^{-1} .

Determination of Ammonia Content

The residual concentration of ammonia after adsorption by 'varying dosage of TABC, varying temperature and time as proscribe by design expert' was determine in the filtrates using the Nessler method, were the Multiparameter photometer with COD for water and wastewater (Model HI83306) of ammonia. After transferring 10 ml of the sample into a cuvette, the stopper was replaced. The cuvette was inserted into the

holder, the lid was closed and the machine was zeroed. The cuvette was removed and 4 drops of HI93700A-0 Ammonia low range reagent A, the stopper cap and the stopper were replaced, it was swirled to mix solution. 4 drops of HI93700B-0 Ammonia reagent B was added. The stopper and the cap were replaced and swirled again to mix the solution. The cuvette was inserted into the holder and the lid was closed. It was allowed for a reaction time of three minutes for the reaction to complete. The concentration was then read out in mg/ml on the spectrometer (ASTM, 2004). Same procedure was applied on the NABC.

Data Analyses

The adsorption capacity (q_e) and adsorptive removal efficiency (R_e) were calculated using the concentration difference between the initial concentration and the equilibrium concentration displayed in equations 1 and 2. Where C_o = initial concentration of ammonium, C_e = equilibrium concentration of ammonium, M = mass of adsorbent (ball clay), V = solution volume and R_e = adsorptive removal efficiency (Seliemet *et al.*, 2023).

$$\text{Adsorption capacity } (q_e) = \frac{C_o - C_e}{M} \times V \quad (1)$$

$$\text{Removal efficiency } (R_e) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

To evaluate the adsorption kinetics of ammonium, the pseudo-first order kinetic model and pseudo-second-order kinetic model were employed as shown in equations 3 and 4 where K_1 and K_2 are constants of the equilibrium rate (Ngouateuet *et al.*, 201; Egahet *et al.*, 2019).

$$\text{Pseudo-first order kinetic model: } \log(q_m - q_t) = \log q_m - \frac{k_1}{2.303} t \quad (3)$$

$$\text{Pseudo-second order kinetic model: } \frac{t}{q_t} = \frac{1}{k_2 q_m^2} + \frac{1}{q_m} t \quad (4)$$

Where K_1 and q_m can be obtain from the plot of $\log(q_m - q_t)$ versus (t) which gives $\frac{k_1}{2.303}$ as slope and $\log q_e$ as intercept for the pseudo-first order kinetic model similarly for the pseudo second order, the kinetic constant k_2 and the theoretical q_m can be calculated from the plots of $(\frac{t}{q_t})$ versus (t) .

To further analyze the adsorption mechanism, the Langmuir and Freundlich isotherm models were adopted (Egahet *et al.*, 2019).

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{K_2 q_o} + \frac{C_e}{q_o} \quad (5)$$

A plot between C_e/q_e versus C_e will generate a straight line with a slope of $1/q_o$ and an intercept equals to $1/k_2 q_o$.

$$\text{Freundlich: } \ln q_e = \ln b + \frac{1}{n} \ln C_e \quad (6)$$

A plot of $\ln q_e$ versus $\ln C_e$ produces a straight line with a slope = $1/n$ and intercept = $\ln b$.

III. Results and Discussion

The surface morphological evaluation of TABC and NABC with SEM at 8,000, 9,000 and 10,000 magnifications respectively is displayed in Figure 1. The result shows typical characteristic morphology such layered or tubular slices pores which are more visible in TABC compared to NASC, implying TABC provides more reactive sites, which enhanced adsorption capacity. The stratification and abundant folds of clay minerals are conducive to the penetration of water, enabling facile adsorption of ammonium likewise, the compact tubular crystals and mono-disperse particle size on the surface, increases the surface-active site of the adsorbent for adsorption (Ahmed *et al.*, 2015; Fan *et al.*, 2021).

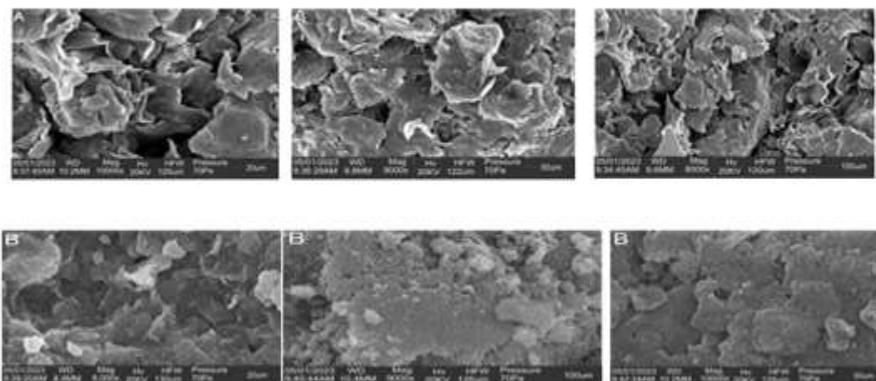


Figure 1: Scanning Electronic Microscope of TABC (A) and NABC (B) At 8,000, 9,000 and 10,000 magnification

FT-IR Analysis of Adsorbents

The FT-IR analysis is important in identification of surface functional groups which plays a great role in adsorption mechanism of ammonia and other adsorbates (Kibamiet *et al.*, 2014). Good adsorbents have specific properties such as large pores, availability of oxygen, hydrogen content and Hydroxyl group (Kibamiet *et al.*, 2014). The FT-IR was carried using the KBr disk method (Johariet *et al.*, 2014).

The FT-IR spectrums of TABC and NABC have similar features as shown in Table 1. The broad peak at 3394.00 and 3400.00 cm^{-1} in TABC and NABC were within the frequency range of (3000 - 4000 cm^{-1}) and is due to stretching vibrations of O-H group from hydroxyl groups (Mohammad *et al.*, 2010). The peaks at 2353.51 cm^{-1} , and 2070.00 cm^{-1} are an indication of organic impurity in the thermally activated ball clay sample. The bands at 1633.33 cm^{-1} and 1633.70 are attributed to C = C stretching of an alkene group in both TABC and NABC as displayed in Table 2 (Faye and Fernandez, 2014). While the 1388.00 and 1386.00 cm^{-1} were within 1390 to 1380 cm^{-1} denoting C-H bending of an aldehyde group. The broad band at 1033.45 and 1031.00 cm^{-1} are attributed to S=O stretching vibration (Arokeet *et al.*, 2013). The characteristic sharp bands at 912.26 cm^{-1} for TABC and 914.43 cm^{-1} for NABC respectively falls within (950-910 cm^{-1}) synonymous to O-H bending of carboxylic acid (Ahmed *et al.*, 2015). The peaks at 668.00 and 667.00 cm^{-1} are attributed to C-H bending in alkynes while the peaks at 535.00 and 541.00 cm^{-1} are attributed to C-Br stretching. The peaks at 428.00 cm^{-1} and 360.22 cm^{-1} are attributed Al-O-Si octahedral vibration (Moradiet *et al.*, 2015).

Table 1: FT-IR Analysis of Thermally Activated and Non-Activated Ball Clay

Group Freq (cm^{-1})	Compound Class	TABC (cm^{-1})	NABC (cm^{-1})	Assignment
3600-3200 (broad)	Alcohol	3394.00	3400.00	O-H stretch
1670-1600	Alkenes	1633.33	1633.70	C=C stretch
1390-1380	Aldehyde	1388.00	1386.00	C-H bend
1070-1030	Sulfoxide	1033.45	1031.00	S=O stretch
950-910	Carboxylic Acid	912.26	914.43	O-H bend
700-610	Alkynes	668.00	667.00	C-H bend
600-500	Alkyl halides	535.00	541.00	C-Br Stretch
500-300	Clay mineral	428.00	466.00	Al-O-Si Vibration

TABC = Thermally activated ball clay; NABC = Non-activated ball clay (Sigma Aldrich)

Batch Adsorption Experiments

The Design Expert version 13[™] recommends 25 experimental runs for ammonia removal in aquaculture effluent within the varying conditions: temperature (25 - 45°C), dosage of ball clay adsorbent (0.5g - 5g), varying pH (3 - 11) and contact time (30 - 90 minutes) with the corresponding residual ammonia content after adsorptive removal as demonstrated in Table 2.

The optimum condition for the adsorptive removal of ammonia in the effluent by both TABC and NABC was achieved at a temperature of 45°C, dosage of 0.5g, pH of 7 and contact time of 60 minute with

removal efficiencies of 98.63014% and 98.35616% for TABC and NABC respectively. In a similar studies, Aziz *et al.*(2019) recorded a lower removal efficiency of 80.55% in aquaculture effluent by ball clay at temperature of 55°C, time of 60mins, pH of 7 and dosage of 0.2 g, suggesting that the conditions of 45°C temperature, dosage of 0.5g, pH of 7 and contact time of 60 minute proscribed by the design expert gave a better removal efficiency.

Table 2: Experimental Runs and Residual Content of Ammonia after Adsorptive Removal

Experimental Runs	Temperature (°C)	Dosage (g)	pH	Time (mins)	TABC. Ce(mg/ml)	NABC. Ce(mg/ml)
1	45	2.75	11	60	0.1	3.65
2	35	0.5	11	60	3.65	3.65
3	45	2.75	7	90	0.17	3.65
4	25	5	7	60	0.09	3.65
5	45	0.5	7	60	0.05**	0.06**
6	35	2.75	11	90	0.12	3.65
7	35	2.75	7	60	0.11	3.65
8	45	2.75	3	60	3.65	3.65
9	35	5	7	30	0.13	3.65
10	35	2.75	3	90	3.65	3.65
11	25	0.5	7	60	0.12	0.17
12	35	0.5	3	60	3.65	3.65
13	25	2.75	3	60	3.65	3.65
14	25	2.75	11	90	3.65	3.65
15	35	5	3	90	0.18	3.65
16	25	2.75	7	90	3.65	3.65
17	35	5	3	60	3.65	3.65
18	35	5	11	60	3.65	3.65
19	25	2.75	7	30	3.65	3.65
20	45	5	7	60	0.16	3.65
21	35	2.75	3	30	3.65	3.60
22	35	0.5	7	90	0.1	3.65
23	35	2.75	11	30	0.07	0.81
24	35	0.5	7	30	0.26	0.21
25	45	2.75	7	30	0.13	3.65
Initial Concentration					3.65	3.65

TABC = Thermally activated ball clay (adsorbent), NABC = Non-activated ball clay (adsorbent), Ce = Residual concentration

The amount of ammonia removed from the aqua cultural effluent and the removal efficiency range from 3.39mg/mL (92.87%) to 3.60 mg/mL (98.63%) by TABC against the 0.05 mg/mL (1.369%) to 3.59 mg/mL (98.35%) for NABC displayed in Table 3; with the corresponding adsorption capacities TABC (0.678 – 0.720) and NABC (0.0018 – 0.718) respectively. The values of the aforementioned parameters suggest a better adsorptive removal efficiency of ammonium when the adsorbent is modified or thermally activated as reported by Wang *et al.* (2018). The performance also corresponds to the morphological porosity exhibited by TABC compared to NABC as revealed in SEM analysis.

Table 3: Adsorption Capacity and Removal Efficiency of TABC and NABC

Adsorbent	Residual Conc. (mg/mL)	Amount of Ammonia Adsorbed (mg/mL)	Adsorption Capacity(mg/g)	Adsorption Efficiency
TABC	0.05	3.60	0.720	98.63%***
	0.12	3.53	0.706	96.71%
	0.07	3.58	0.716	98.08%
	0.26	3.39	0.678	92.87%*
	0.1	3.55	0.120	97.26%
	3.65	0	0	0
	0.17	3.43	0.126	95.34%
	0.09	3.51	0.071	97.53%
	0.11	3.54	0.128	96.98%
	0.13	3.52	0.070	96.43%
	0.18	3.47	0.069	95.06%

	0.16	3.49	0.698	95.61%
NABC	0.06	3.59	0.718	98.35%***
	0.17	3.48	0.696	95.34%
	0.81	2.84	0.568	77.80%
	0.21	3.44	0.688	94.24%
	3.65	0	0	0
	3.60	0.05	0.0018	1.369%*

KEY:Ce = Equilibrium/Residual Concentration, Qe = Adsorption capacity, Re = Efficiency of adsorption, TABC = Thermally activated ball clay, NABC = Non-activated ball clay.

Effect of pH on Adsorption of Ammonia

The optimum condition for the adsorptive removal of ammonia in the effluent by both TABC and NABC was achieved at a temperature of 45°C, dosage of 0.5g, contact time of 60 minute and pH of 7 with removal efficiencies of 3.6mg/mL (98.63014%) and 3.59mg/mL (98.35616%) for TABC and NABC respectively. From the result obtained, it was observed that optimum removal was achieved at pH of 7 which may be due to increase in electrostatic attraction between the adsorbate and adsorbents (Bolattet al., 2010; Sha’Atoet al., 2018). However, as shown in Figure 2; when the pH approaches alkaline at 11, there was an observed decrease in mean amount of ammonia adsorbed from 2.932 mg/mL to 1.777 mg/mL for TABC while from 0.875 mg/mL to 0.473 mg/mL for NABC respectively due to repulsion between the adsorbate - adsorbent surface (Denizliet al., 2001).

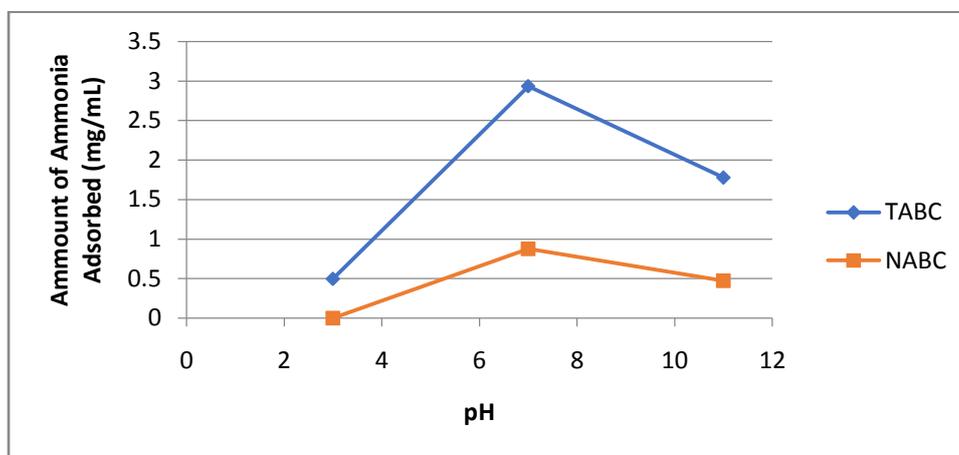


Figure 2: Effect of pH on Adsorption of Ammonia

Effect of Adsorbent Dosage on Ammonia Adsorption

The effect of adsorbent dosage (TABC and NABC) on the removal of ammonium as seen in Figure 3; Since the optimum removal of ammonium was achieved at 0.5g adsorbent dosage when subjected to temperature of 45°C, pH of 7 and contact time of 60mins with mean adsorptive removal of 2.34 mg/mL and 1.75 mg/mL by TABC and NABC respectively. However, considering the same aforementioned factors, as the dosage increased from 0.5g to 5g. The percentage adsorptive removal of ammonium decreased, most likely due to saturation of sorption sites which were initially available by ammonium (Nanganoaet al., 2014).

For instant, as the amount of adsorbent increases from 0.5 g to 2.7 g, the mean removal of ammonium decreased from 2.34 mg/mL to 1.631 mg/mL then an increase to 2.34 mg/mL for TABC. The trend for the NABC was a decrease in the mean amount of ammonium removed from 1.752 mg/mL to 0.598 mg/mL at 0.5g to 5.0g adsorbent dosage demonstrated in Figure 3.

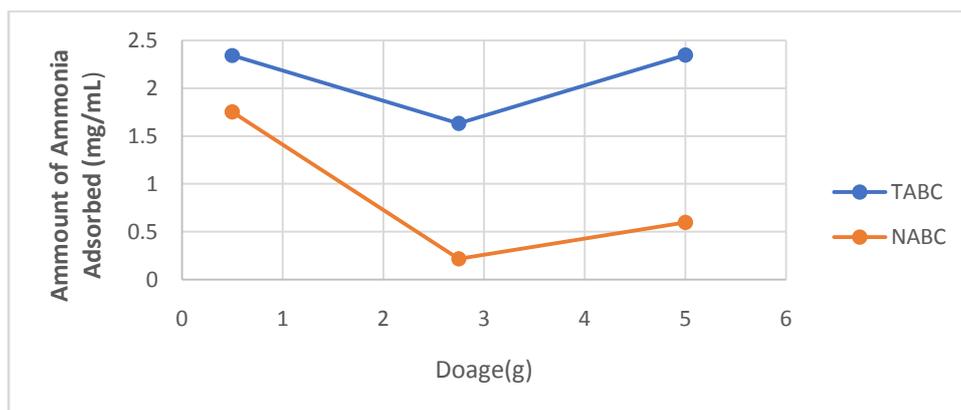


Figure 3: Effect of Adsorbent Dose on Adsorption of Ammonia

Effect of Temperature on Ammonia Adsorption

Figure 4: shows the effect of temperature on adsorption of ammonia suggesting that as the temperature increases from 298K - 318K, the mean removal of ammonium also increases from 1.182mg/mL to 2.94mg/mL for TABC while that of NABC decreased from 0.598mg/mL to 0.58mg/mL. This may be attributed to increase in collision between the adsorbent and the adsorbate (Kannan *et al.*, 2009). Comparatively, TABC was found to be a more potent adsorbent than the NABC which may be attributed to its activated porosity during calcination and high surface charge.

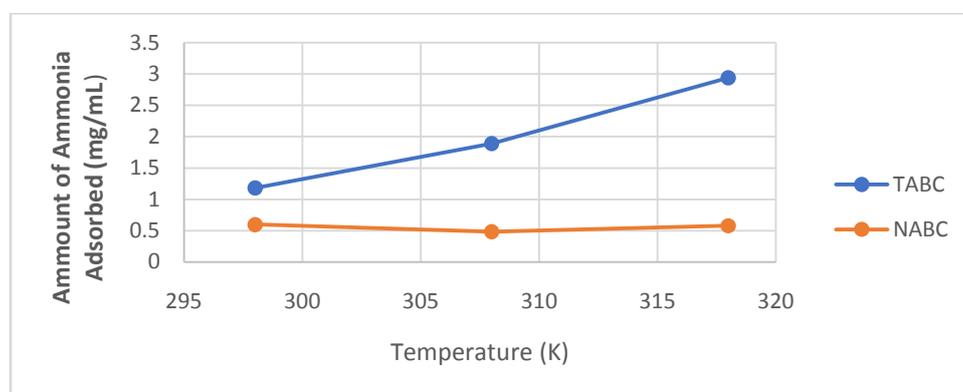


Figure 4: Effect of Temperature on Adsorption of Ammonia

Effect of Contact Time on Ammonia Adsorption

Effect of contact time on ammonia adsorption as presented in Figure 5, it was observed that adsorption capacity increased from (30 – 90 minutes) until equilibrium was attained at 90 minutes. Adsorption rate appeared to be very fast in the first 30 minutes, which could be explained to high number of adsorption sites from the start (Ahmed *et al.*, 2015). As the time increased, the adsorption sites became gradually saturated until equilibrium was attained at 90 minutes (Riebe and Bunnenberg, 2007). At 90 minutes, the highest adsorption capacity of 2.802 mg/g, and 1.047 mg/g were observed for TABC and NABC respectively. This may be due to the gradual saturation of the active sites by ions as the contact time increased (Bhattacharyya and Gupta 2011). This is in agreement with a study reported by Yaqoob *et al.* (2017) which found that the optimum time for ammonia absorption using activated carbon as adsorbent was 60mins, while on the contrary, a study by Wang *et al.* (2018) found that the optimum time for ammonia adsorption using zeolite as adsorbent was 180 minutes.

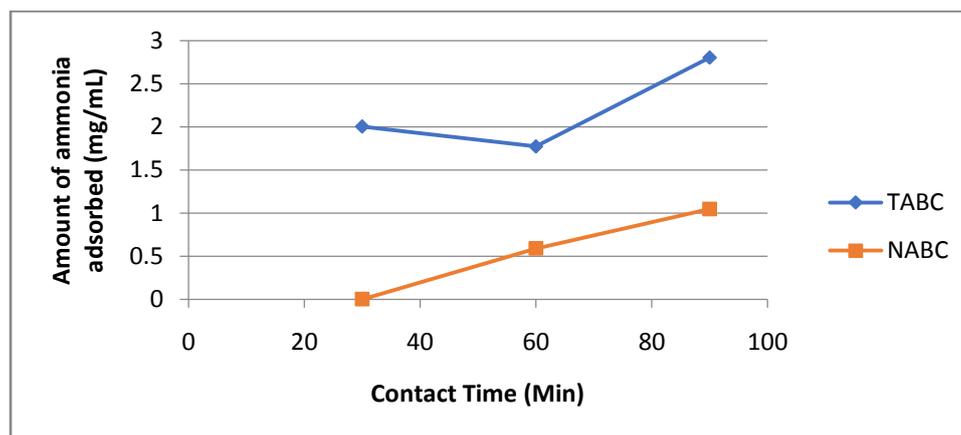


Figure 5: Effect of Contact Time Adsorption of Ammonia

Adsorption Kinetic Analysis

Data obtained from the effect of contact time on adsorption of ammonia were fitted into the pseudo first order, second order kinetic models and the kinetic parameters displayed in Table 4. The results showed that the sorption of ammonia on TABC and NABC could be described by both first and second order kinetic model. From their correlation coefficient R^2 , it was observed that the Blanchard pseudo-second order gave better fittings for with R^2 values ranging from 0.9982 - 0.9993 as compared with the Lagergren pseudo-first order which gave lower R^2 values ranging from 0.9158 - 0.9777 and the pseudo-second order rate constant K_2 was in the range 0.158 - 0.159 $\text{g.mg}^{-1}\text{min}^{-1}$. The high value of R^2 for the second - order shows that the pseudo second order best describes the whole adsorption processes indicating that chemisorption is predominant on all adsorbents as the rate determining step (Ajay *et al.*, 2015). This is in agreement with the report by Aziz *et al.* (2019) in his quest to remove ammonia in waste water effluent using ball clay.

Table 4: Kinetic Parameters for Adsorption Lagergren First Order and Blanchard Second Order for Ammonia

Model	Parameters	TABC	NABC
First Order	K_1 (min^{-1})	0.0184	0.0290
	Q_e (mg/g)	0.00055	0.02055
	R^2	0.9777	0.9158
Second Order	K_2 (min^{-1})	0.158	0.159
	Q_e (mg/g)	0.0732	0.0699
	R^2	0.9993	0.9982

Adsorption Isotherm Evaluation

Data's generated were fitted into both the Langmuir and Freundlich isotherms models where the isotherm parameters obtained presented in Table 5. Langmuir isotherm revealed correlation coefficients R^2 values of 0.9679 and 0.9737 for TABC and NABC while Freundlich isotherm gave a lower value of 0.6497 and 0.7267 for TABC and NABC respectively. The results indicate that ammonium removal by TABC and NABC best obeyed Langmuir isotherm. This implies that the Langmuir model best described the experimental data and can be concluded that the active sites on the adsorbents surface were homogeneously distributed and forms a monolayer adsorption (Baiet *et al.*, 2010; Nanganoaet *et al.*, 2014).

The theoretical values of Langmuir constants Q_m and K_L were calculated from the slope and intercept of a linear plot of $1/Q_e$ versus $1/C_e$ respectively. The result in Table 5, gave Q_m values of 0.0728 mg/g, and 0.0721 mg/g for TABC and NABC respectively. These values indicate the total number of binding sites that are available for adsorption (Ajay *et al.*, 2015). From the values of the Langmuir isotherm calculated from the experimental data with the dimensionless constant called separation factor, R_L , the values were found to be all < 1 and > 0 indicating a favorable adsorption for all adsorbent (Krishna and Swamy, 2012).

Even though, the mechanism is best explained by the Langmuir isotherm, the Freundlich isotherm which is based on the assumption that adsorption takes place on heterogeneous surface of the adsorbent (Nanganoaet *et al.*, 2014). From the Freundlich model parameters in Table 5, K_F value of 0.0027 mg/g was obtained for TABC is greater than the 0.0024 mg/g value for NABC; suggesting that TABC is more potent for adsorption of ammonium (Krishna and Swamy, 2012). Also, the adsorption is favorable for values > 1 and unfavorable for values < 1 for the adsorption intensity n_F (Dawoduet *et al.*, 2012). This indicates that adsorption is favorable for ammonia. Adsorption is homogenous rather than heterogeneous due to the lower R^2 values

obtained from Freundlich isotherm (Nanganoaet *al.*, 2014). From the results obtained, the $1/n$ values was found to be < 1 suggesting the adsorption processes are favorable for adsorption (Sha'Atoet *al.*, 2018).

Table 5: Isotherm Parameters for Ammonia Adsorption on Adsorbents

Model	Isotherm Parameters	TABC	NABC
Langmuir Isotherm	Qm (mg/g)	0.0728	0.0721
	K_L	0.9455	1.3786
	R^2	0.9679	0.9737
	R_L	0.2274	0.1559
Freundlich Isotherm	K_F	0.0027	0.0024
	R^2	0.6497	0.7267
	$1/n$	0.0481	0.0279
	n_F	20.790	35.842

IV. Conclusion

Thermally activated ball clay (TABC) and Non-activated ball clay (NABC) exhibited good physicochemical attributes as adsorbents for the effective adsorptive removal of ammonia from aquaculture effluent. The adsorptive removal of ammonium by TABC and NABC varies with the reaction condition such as time, pH, temperature, adsorbent dosage. However, the optimum removal was 98.63% and 98.35% efficiency within the condition of temperature 318K, pH of 7, and dosage of 0.5 g and contact time of 60 minutes for TABC and NABC. Mechanism of the removal process best fit the linearized Langmuir isotherm than the Freundlich isotherm suggesting a monolayer adsorption. Likewise, the kinetic pathway implies that chemisorption dominates the rate limiting step since Kinetic data fitted the pseudo-second order model than first order. Based on the results obtained in this study, thermally activated ball clay is hereby recommended as a viable option for the removal of ammonia contaminant from aqua cultural effluent. However further studies can be carried out on the various modifications of ball clay to find out the best modification for ammonia removal.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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