Combination of *Moringa oleifera* Seed Powder and Iron Sulfate Heptahydrate Salt as Biopolymer Based Matrix for Application as Adsorbent for Odor Inhibition in Poultry Farms

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ABSTRACT: A biopolymer based matrix of *M. Oleifera* Seed Powder (MOSP) and Ferrous Sulphate Heptahydrate (FSH) salt was formulated as adsorbent for odor inhibition in poultry farms. The matrix was characterized using FT-IR technique and its performance as adsorbent for NH_4^+ removal from aqueous solutions was examined via sorption studies. The result showed an excellent sorption performance at 0.1 g sorbent dosage, pH of 9 and 30 min agitation time. This indicates that the matrix possess an excellent ion exchange property and thus a suitable sorbent for NH_4^+ even in low concentration environment. The study reveals the capacity of the adsorptive matrix as a safe and cost-effective method to be used for ammoniacal odor control from poultry farms which may be applicable to other animal farm operations (AFOs).

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Ammonia is generated and dispersed into the environment from industries and animal feeding operations (AFOs). Its presence constitute odor nuisance as an immediate impact on the population. In its ionic form, (NH_4^+) ion, it is also the most commonly encountered nitrogenous compounds in waste waters, resulting in eutrophication of water bodies which is a major global environmental issue Yiang and Aiqin (2009). Its major source is excessive nutrients from run offs of over fertilization of farm lands especially with animal waste. In poultry houses, NH_3 is said to lower bird performance and increase disease susceptibility (Beker *et al.,* 2004). In the birds, $NH_4 – N$ is excreted as uric acid which is quickly converted into NH_3 at pH above 7.0. Below pH 7.0, NH_3 exists predominantly as NH_4^+ and is not volatilized (Ritz, 2004). Protonation of NH_3 into nonvolatile ammonium (NH_4^+) therefore requires an acidic environment. In this work, an acidic biopolymer based matrix is developed to provide for this condition. Also the structure of the matrix showed

functional groups capable of binding NH_4^+ on the surface through electrostatic interaction thus preventing its conversion to NH_3 and subsequent volatilization (Haiwei *et al.,* 2010) thereby inhibiting ammoniacal odors. Technologies such as biofiltration and scrubbing to clean exhaust air from poultry houses have been employed. Odor and moisture absorbents have been based on clay products containing zeolites and hydrous silicates that act as exchangers and absorbents (Ritz *et al.,* 2004; Pandharipade *et al.,* 2012; liu *et al.,* 2010). Other methods for the removal of NH_3-N include Chemical precipitation and Membrane Technology (Ahmadianiannimini *et al.,* 2017) as reported in Zahrim *et al.,* 2018. The removal of NH_4^+ ion from waste waters and sludge using natural and biopolymer composites have been demonstrated (Haiwa *et al.,* 2010; Yian *et al.,* 2009; Du *et al.,* 2005; Gunnay *et al.,* 2007). However, the application of these technologies has been limited by cost, size, performance and technical problems. The low cost iron impregnated bio-based matrix

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formulated and characterized in this work showed immense potential in stabilizing NH_4^+ ion in aqueous solution. The highly acidic nature of the matrix is advantageous since pH levels below 5.0 are reported to provide hostile conditions for microbes which enhance inhibition of ammonifying and putrefying bacteria. This will prevent premature manure degradation that would lead to loss of nutrients and odor generation. It therefore has the promise of large scale application in binding NH_4^+ especially in poultry farms in the developing countries like Nigeria where poultry production is highly proliferated with poorly managed facilities. Hence, the objective of this paper is to evaluate the performance of a biopolymer based matrix of *M. oleifera* Seed Powder (MOSP) and Ferrous Sulfate Heptahydrate (FSH) salt for application as adsorbent for odor inhibition in poultry farms.

MATERIALS AND METHODS

Materials: M. Oleifera pods were obtained from a personal farm in Girei Local Govt area of Adamawa state. The pods were deshelled to obtain the seeds which were then sun dried for five days. They were finally ground into a fine powder in a micro hammer mill (Polymix PX – MFC Kinematica AG). Ferrous sulfate heptahydrate was obtained from Northern Scientific Co ltd and used without further purification.

Preparation and Characterization of the biomatrix: The MOSP was then oven dried at 105^0C for 12hrs. The dried MOSP was again pulverized on the micro harmer mill using a 300mm mesh size. The powder was washed in distilled water (DW) to remove soluble impurities and adhered foreign particles. It was dried at 105^0C for 12hrs. The Iron (II) salt was also dried at standard conditions. The dried materials were blended into the matrix through factorial experiment as described in our earlier work (Manu *et al.,* 2013). The optimum formulation was selected and characterized using FTIR technique and its performance as adsorbent for NH_4^+ removal from aqueous solutions was examined via sorption studies.

Sorption Studies: Batch adsorption experiments were carried out under various absorption parameters (solution pH, dose, solution concentration etc). Appropriately weighed adsorbent (0.1 – 1.0 g) was placed in 25m conical flask. 25ml of sorbate containing varying amount of analyte (0.1 – 1.5 mg/L) was added and then Stoppard. The flasks were fitted to an orbital shaker at a certain agitation speed (100rpm) for a specific time period (2-8hrs) pH of the solutions was adjusted to the required value by adding either 0.1N HCl or 0.1N NaOH respectively. Initial and final concentrations of NH_4^+-N, in the filtrate were

measured according to Nessler's reagent calorimetric method (Yian *et al.,* 2009). The adsorption capacity for NH_4^+ - N was calculated using the following equation (Abd El Latif *et al.,* 2010):

$$g = (Co - Ce)V/m$$

Where: q=absorption capacity of NH_4^+ onto absorbent (mg/g); C_o=initial NH_4^+ concentration (mg/l); C_e=equilibrium NH_4^+ concentration; m=mass of absorbent used (g); V=Volume of NH_4^+ solution used (L)

Effect of pH: The effect of pH on % soption of NH_4^+ onto matrix was investigated over the range (1-12) using 25ml solution volume, 30min agitation time, 0.5m, 100rpm and 0.1 g sorbent dose. The pH was adjusted to desired value by 0.1N HCl or 0.1N NaOH.

Effect of absorbent dosage: In order to study the influence of absorbent concentration (0.1 – 1.0g) on the uptake of NH_4^+ unto matrix, 25ml of a certain solute concentration, 30min agitation time and 100rpm were used at a pH of 9 at room temperature (30^0C).

Agitation time/speed: Agitation time was varied from 20-120 min. 25ml of solute concentration; 100 rpm agitation time and a pH of 9 were used at room temperature (30^0C).

Concentration of adsorbate: A sorbate concentration range of 2-25 mg/L was used to study the effect of sorbate concentraton on the NH_4^+ adsorption onto the matrix. The study was done under optimized conditions of 0.1g sorbent dose, $25cm^3$ solution, 30min agitation time and pH 9.

RESULTS AND DISCUSSION

FTIR Analysis: The seeds of *moringa oleifera* is reported to be rich in proteins, fats and crude fibre (Compaore *et al.,* 2011; Kawo *et al.,* 2009) which may contain polar functional groups such as – NH_2; -COOH, - OH. These groups might have the abilities to bind some pollutants in an adsorption process (Pagnamelli, *et al.,* 2003). FTIR analysis was carried out on plain MOSP and Iron impregnated MOSP (matrix) using FTIR-8400 Shimadzu, Japan, to identify the functional groups that may relate to the adsorption process. The broad and strong band ranging from 2900 to 3500 (Fig. 1) may be due to – OH stretching vibration and peaks at 1000-1500 are a result of bending vibration of the surface O-H bond. The peaks around 1651 correspond to the C = O stretching. The peaks at 1432 and 1245 are due to vibrational movement of C – H or CH (Sun et al, 2005).Figure 2 represents the FTIR of Iron modified

MOSP. Comparing this spectrum with the spectrum of plain MOSP (Figure 1), the wave number shifted from 3379, 2925, and 1651 to 3350, 2926 and 1647. The peaks represent – OH and – COOH groups, which presence signifies that the sample surface is negatively charged. The total number of the charges depends on the amount of these groups attached on the sample surface (Feng et al., 2009).From the FTIR spectra of MOSP and matrix, it is evident that peaks at 3257, 1245 and 786 cm^{-1} disappeared. We simply ascribe this to the electrostatic interaction of Fe with OH group of MOSP.

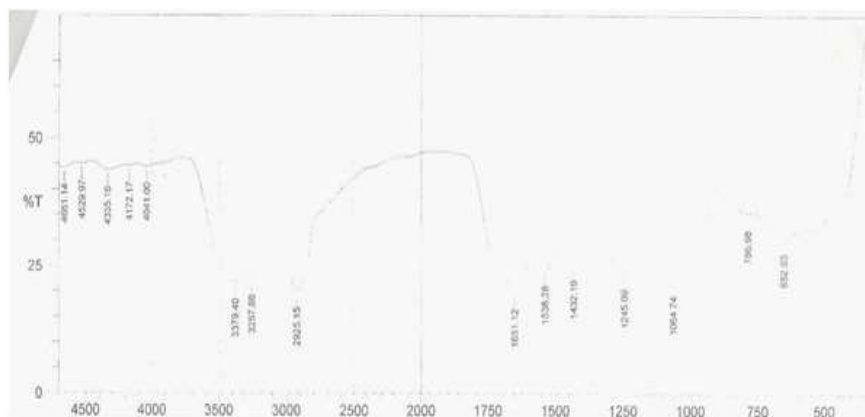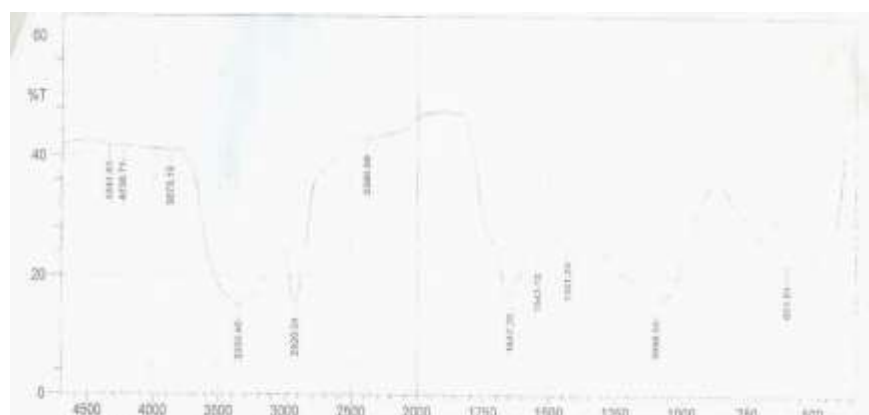**Fig 1:** FTIR of plain MOSP

Fig 2: FTIR of matrix

Effect of pH: PH affects the surface charge of the adsorbent and thus an important factor that would control adsorption of NH_4^+ onto the adsorbent surface and therefore is necessary to be studied. Change in pH affects the adsorptive process through dissociation of the functional group on the adsorbent surface active sites (Abdel, 2010). As the pH increases, the negative charge on the adsorbent also increases. This would cause the following change on the surface of the matrix:

$$Cell - OH + OH^- \rightarrow Cell - O^- + H_2O \quad (1)$$
$$RCOOR + OH^- \rightarrow RCOO^- + ROH \quad (2)$$
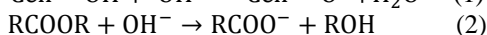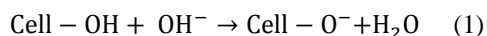
The presence of OH and COOH groups may confer negative charges on the surface of the matrix. Therefore the NH_4^+ adsorption may relate to these groups and is expected to increase.

$$Cell - O^- + NH_4^+ \rightarrow Cell - O.NH_4^+ \quad (3)$$
$$RCOO^- + NH_4^+ \rightarrow RCOO^-NH_4^+ \quad (4)$$
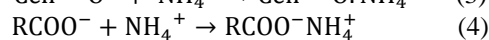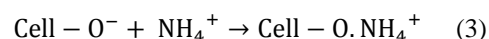
From Figure 3, the % sorption was seen to increase with pH. The highest % sorption was achieved at pH 9. The optimum pH range was however $3 - 9$. For the pH above 9, ammonium adsorption flattened and may even decrease further, while at pH below 5, the amount decreased. This may be due to adsorbent site competition of the adsorbate with H^+ ions. At higher pH values, NH_4^+ ions tend to be transformed into aqueous NH_3. However, at higher pH levels, increase in negative charge on the adsorbent surface increases the adsorption of cationic adsorbates (DO Gan et al., 2004).
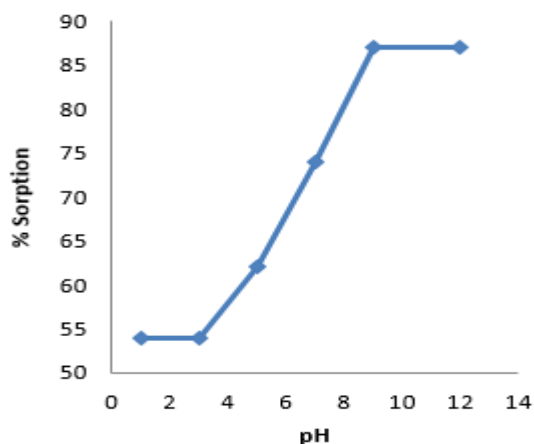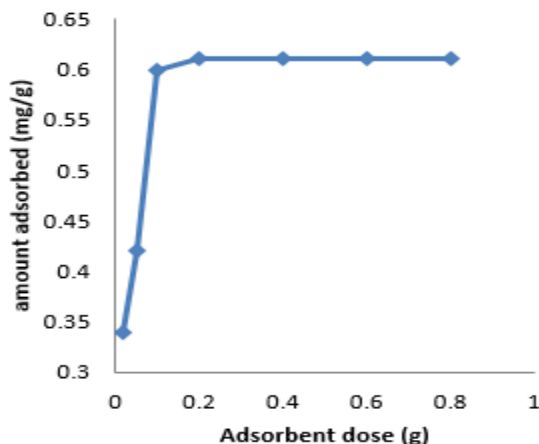
Fig 3: Effect of pH on the % sorption of NH_4^+ in the range (1–12) onto 0.1 g MOSP, 25 cm^3 of 0.5 mol dm^{-3} solution concentration of sorbate, and 30 min agitation time at 30^0C.

Fig 4: Effect of adsorbent dose on the adsorption of NH_4^+ onto matrix of MOSP (0.02–0.8 g using 25 cm3 of 0.5 mol dm^{-3} solutionconcentration of sorbate respectively at 30 min agitation time, pH 9 and 30^oC.

The high % sorption of NH_4^+ ion suggests that the adsorbent possess very strong ammonium binding capacity which prevents the shift to ammonia under alkaline conditions. Previous studies have shown that optimum pH ranges for ammonium adsorption unto Zeolite, clinoptilolite and volcanic tuff were 5-8, 5-7 and 7-8 respectively (Karadag et al., 2007; Ji et al., 2007). The expanded pH range (3-9) exhibited by the matrix indicates a promising new source of odor adsorbent.

Effect of adsorbent dosage: The adsorbent dose represents an important process parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of the adsorbate. In order to investigate the effect of sorbent concentration(0.02–0.8 g) on the sorption of NH_4^+ onto matrix, 25 cm^3 of 1mg/L NH_4^+, 30 minagitation time were employed at pH 9 and ambient temperatures. The relationship between sorbent dose and percent sorption is depicted in fig. 4.From the figure, a sharpincrease in % sorption was observed from 0.05 to 0.1 g ofsorbent amount whichremained almost constant from 0.2 to 0.8 g, suggesting 0.1 g tobe the sufficient sorbent dose to accommodate all the sorbatemolecules.

However the sorption capacity of NH4+ unto the matrix does not show significant increase with increase of sorbent dosage. The phenomena can e attributed to unsaturation sorption sites and particle aggregation (Ma *et al.,* 2012). This result corroborates the results of previous studies involving the use of sawdust in the removal ofunwanted materials from aqueous solution (Han *et al.,* 2006).

Effect of agitation time: The effect of contact time on the adsorption of NH_4^+ onto matrix adsorbents was investigated (Figure 5).
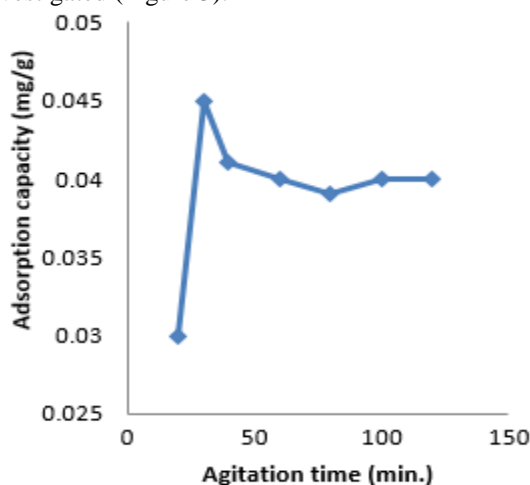
Fig 5: Effect of agitation time 20–120 min on % sorption of NH_4^+ onto 0.1 g MOSP, 25cm^3 of 0.5 mg/L solution concentration of sorbate at pH 9 and 30^oC.

From Figure 5, it can be seen that the uptake of NH_4^+ by adsorption on matrix was found to be rapid in the first 30min. and then slowed down as agitation time increased. A possible explanation may be that the fast diffusion onto the external surface was followed by fast pore diffusion into the intra-particle matrix due to the Vander Waals forces and electrostatic attractions between the NH_4^+ molecule and the adsorbent.

Effect of sorbate concentration: The effect of NH_4^+ concentration (Fig. 6) on its uptake by matrix was examined under optimized conditions of 0.1 g sorbent dose/25 cm^3 solution using 30 min agitation time and pH 9.
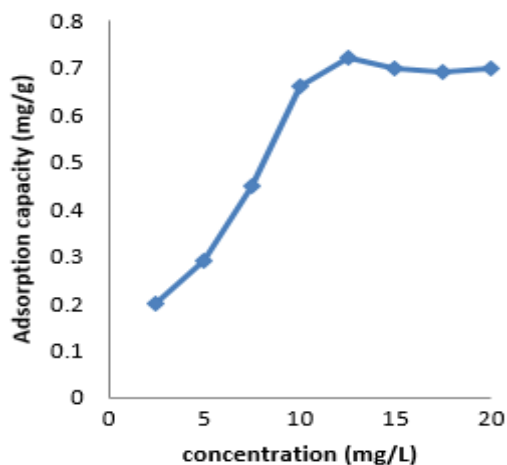
Fig 6: Effect of NH_4^+ concentration in the range of $2 - 25$mg/L /25 cm3 of sorbate on its sorption onto 0.1 g MOSP, 30 min agitation time at pH 9 and 30°C.

It can be seen from the Figure that the amount of NH_4^+ adsorbed (mg/g) occurred rapidly and efficiently at low ammonia concentration and remained constant at equilibrium value with increased initial NH_4^+ concentration, corroborating the studies by Mohd *et al.,* 2021. At lower sorbate concentrations, there remain unsaturated adsorption sites, leading to increased adsorption until equilibrium. At equilibrium, no further sorption occurs due to limited sites on the sorbate surface. Sorbate concentration is reported to provide an important driving force to overcome all mass transfer resistance of the sorbate between the aqueous and solid phases (Ho, 2005). Hence a higher initial concentration of sorbate will enhance the adsorption process. Moreover the higher ammonia adsorption capacity exhibited by the matrix is mainly attributed to the excellent ion exchange property possessed by the biopolymer matrix. The result indicates that the matrix is a suitable adsorbent even in low ammonia concentration environment.

Conclusion: This study examined the capacity of the biopolymer based matrix as an adsorbent for stabilizing NH_4^+ in aqueous solutions. The study showed that the matrix possess an excellent ion exchange property and thus a suitable sorbent for NH_4^+ ion. Since NH_4^+ is the most commonly encountered nitrogenous compound in poultry farms and other animal feeding operations which presence constitutes odor nuisance, the application of this adsorptive matrix could be a save and cost effective means for ammoniacal odor control from these facilities.

REFERENCES

Abd El-Latif1, MM; Amal, MI (2010). Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite. *J Am Sci*6 (6): 267 – 283

Ahmadiannamini, P; Eswaranandam, S; Wickramasingle, R (2017). Mixed matrix membranes for effective ammonium removal from wastewaters. *J. Membre. Sci*. 526: 147-155.

Beker, A; Vanhooser, SL; Swartzlander, JH (2014). Atmospheric ammonia concentration effects on broiler growth and performance. *J. Appl. Poult. Res.* 13:5-9.

Bulut, Y; Aydın HA (2006).Kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*. 194(1-3):259–267

Compaoré, WR; Nikièma, PA; Bassole, HI (2011). Nutritional Properties of Enriched Local Complementary Flours. *Adv. J Food Sci. Technol.* 3(1): 31-39.

Doˇgan M; Alkan M; Demirbas O (2004). Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions. *Chem. Eng. J.* 124:89–101.

Du, Q; Liu, S; Cao, Z (2005). Ammonia removal from aqueous solution using natural Chinese clinoptilolite. Sep. *Purif. Technol*. 44(3):229-234

Feng, N C; Guo, X Y; Liang, S (2009). Adsorption study of copper (II) by chemically modified orange peel. *J. Hazard Mater*. 164: 1286–1292.

Gunay, A (2007). Application of nonliner regression analysis for ammonium exchange by (Bigalic) clinoptilolite. *J. Hazard. Mater.* 148(3):708-713.

Haiwei, L; Yuanhua, D; Haiyun, W (2010). Adsorption behavior of ammonium by a bioadsorbent – Boston ivy leaf powder.*J. Environ. Sci.* 22(10): 1513–1518

Han, RP; Zou, WH; Zhang, ZP; Shi, J (2006). Removal of copper (II) and lead (II) from aqueous solution by manganese oxide coated sand. I. Characterization and kinetic study. *J. Hazard. Mater.* 137:384–395.

Ho, YS; Chiang, TH; Hsueh, YM (2005). Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochem.* 40:119–124.

Ji, ZY; Yuan, J S; Li, XG (2007). Removal of ammonium from wastewater using calcium form clinoptilolite. *J. Hazard Mater.* 141: 483–488.

Karadag, D; Koc, Y; Turan, M (2007). A comparative study of linear and non-linear regression analysis for ammonium exchange by clinoptilolite zeolite. *J. Hazard Mater.* 144: 432–437.

Kawo, AH; Abdullahi, BA; Gaiya, ZA (2009). Preliminary phytochemical screening, proximate and elemental composition of *Moringa oleifera* lam seed powder. J. *Pure Appl. Sci.* 2(1): 96 – 100.

Lin, H; Dong, Y; Wang, H (2010). Adsorptive behavior of ammonium by a bioadsorbent-Boston ivy leaf powder. *J. Environ. Sci.* 22(10): 1513-1518.

Ma, J; Jia, Y; Jing, Y; (2012). Kinetics and thermodynamics of methlylene blue adsorption by cobalt-hectorite composite. *Dyes Pigm* 93, 1441-1446.

Manu, JM; Barminas, J T; Aliyu, B A (2013). Formulation of *Moringa oleifera* Seed Powder and Ferrous Sulfate Heptahydrate into A Matrix to Control Coliform Bacteria and Odor in Poultry Manure. *IJERT, 2 (3): 1-17.*

Mohd, R A; Mohd, HDO; Siti, H; Sheik, A K (2021). Ammonia removal by Adsorptive Clinoptilolite Ceramic Membrane: Effect of Dosage, isothermal behavior and regeneration process. *Korean J. Chem. Eng*. 38(4), 811.

Pandharipade, SL; Yogesh, M; Raj, T (2012). Synthesis of adsorbents from waste materials such as ZiziphusJujude seed and mango kernel. *Int. J. Eng. Res Appl.* 2 (4):1337-1341.

Ritz, CW; Fairchild, B D; Lacy, MP (2004). Implications of Ammonia Production and Emissions from Commercial Poultry Facilities: A Review. *J. Appl. Poult. Res.* 13:684-692.

Sun, X F; Xu, F; Sun, R C (2005). Characteristics of degraded cellulose obtained from steam-exploded wheat straw. *Carbohydr Res*, 340: 97–106.

Yian, Z; Junping, Z; Aiqin, W (2009). Fast removal of ammonium nitrogen from aqueous solution using chitosan-*g*-poly (acrylic acid)/attapulgite composite. *Chem. Eng. J.* 155(1/2): 215–222

Zahrim, AY; Lija, Y; Azreen, I (2018). Adsorption of Ammonia nitrogen by using Jack fruit (Artocarpus heterophyllus) seeds: Batch and fixed bed column studies. *Cur. Environ. Engineer.* 05(3) 202-2010