ISSN (Print) : 0974-6846
Indian Journal of Science and Technology, Vol 10(6), DOI: 10.17485/ijst/2017/v10i6/111221, February 2017 ISSN (Online) : 0974-5645

# Ammonia-Nitrogen Recovery from Synthetic Solution using Agricultural Waste Fibers

**A.Y. Zahrim[1*], L. N. S. Ricky[1], N. Hilal[2] and K. F. Tamrin[3]**

[1]Department of Chemical Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia; zahrim@ums.edu.my, rickylns@hotmail.com

[2]Centre for Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Swansea SA2 8PP, UK; n.hilal@swansea.ac.uk

[3]Department of Mechanical and Manufacturing Engineering, Faculty of Engineering Universiti Malaysia Sarawak (UNIMAS) Kota Samarahan, Malaysia; k.f.tamrin@outlook.com

## Abstract

**Background/Objectives:** In this study, modification of Empty Fruit Bunch (EFB) fibers as a means to recover ammonia nitrogen from a synthetic solution was investigated. **Methods:** The EFB fiber was modified using sodium hydroxide. Adsorption-desorption studies of ammonia nitrogen into the modified EFB fiber were investigated **Findings:** The increase in adsorption capacity was found to be proportional with the increase of pH up to 7, temperature and ammonia concentration. The maximum adsorption capacity is 0.53-10.89 mg/g. The attachment of ammonia nitrogen involves ion exchange-chemisorption. The maximum desorption capacity of 0.0999 mg/g. **Applications:** This study can be used as a baseline for designing a low cost adsorbent system for ammonia nitrogen recovery drainage and industrial wastewater as well as EFBs-palm oil mill effluent composting.

**Keywords:** Ammonia Nitrogen, Agricultural Waste, Desorption, Empty Fruit Bunch, Nutrient Recovery

## 1. Introduction

Industrial nitrogen can be discharged in large volume from pulp and paper, fertilizer, and mining industry[1]. Highest nitrogen discharges in pulp and paper industry is due to pulping and bleaching process[2]. Besides that, agricultural drainage and municipal waste are also among the main sources of polluter[1]. Ammonia nitrogen concentration greater than 10 mg/L causes intensifying of genotoxicity[3]. In addition, nitrogen pollution in waterways results in the eutrophication and fouling of rivers, lakes, water reservoirs and oceans. Recovering ammonia nitrogen from polluted water could be an option in treating the contaminated water and simultaneously recycle the nutrient back for agricultural purposes. Of numerous techniques investigated for ammonia nitrogen recovery[4], a considerable amount of approaches seem to concentrate on developing cheaper and effective agricultural waste adsorbents[5]. This method is considered eco-friendly, economical, and practically simple to operate[6].

In Malaysia, Empty Fruit Bunch (EFB) fibers are abundantly available waste with about 91.2 million tons were produced annually[7]. Previously, EFB fibers compost has shown potential in removing ammonia nitrogen from synthetic solution[8]. Degraded fibers could enhance the sorption of ammonia nitrogen due to increasing in negatively charge surface site. However, EFB biodegradation take a long time to biodegrade. To reduce the modification time, chemical modification is suggested in this study. Modification of pine cone powder using sodium hydroxide was found to increase the ammonia nitrogen sorption capacity to 6.15 mg/g[6]. In another study, adsorption capacity of banana peels treated with sodium hydroxide was found to increase from 8.6 to 20.0 mg/g[9]. However, the common purpose for EFB modification studies reported so far is mainly for the productions

*Author for correspondence

of sugar[10] and bioethanol[11]. Nevertheless, we find that there are limited studies focusing on modification of EFBs fiber for the recovery of ammonia nitrogen. In this study, adsorption-desorption studies of ammonia nitrogen into the modified EFB fiber were investigated and the biosorption isotherm was also determined.

## 2. Materials and Methods

Ammonium chloride salt ($NH_4Cl$) (QRëC™) and distilled water were used for the preparation of a solution of 50 mg $L^{-1}$ ammonia nitrogen solutions. The shredded EFB fibers were collected from Tawau, Sabah. The fibers were subjected to treatment using 10 mM of sodium hydroxide (NaOH) for 12 hours in room temperature. Batch adsorption experiments were conducted using fixed amount 15.71 g of EFB fibers. The effects of pH on adsorption were investigated at various pH values, ranging from 3 to 10. Desorption study was carried out by using 0.1 M HCl and NaOH solutions. The ammonia nitrogen concentration was measured according to volumetric method, known as Nessler Method[12], using UV-vis spectrophotometer (Jasco UV-vis 650) at maximum wavelength of 425 nm.

## 3. Results and Discussion

### 3.1 Sorption Studies

Figure 1 shows ammonia nitrogen removal by various initial concentrations of ammonia nitrogen (0.5, 5, 50, 200, 1500, 4000 mg/L) at 40 minutes contact time. It clearly shows that the amount of ammonia nitrogen being removed increases with initial concentration. This trend is consistent with previous study[13]. According to Figure 1, the highest sorption capacity is 10.893 mg/g at ammonia nitrogen initial concentration of 4000 mg/L. Similarly, higher removal of ammonia nitrogen waste found at high initial ammonia nitrogen concentration using low-cost adsorbents[13,14]. The reason for these finding could be due to high probability of collision between ammonium ions with the surface of fibers especially at high concentration[14].

The effects of temperature on the sorption of ammonia nitrogen onto modified EFB fibers at different contact time are shown in Figure 2. The sorption capacity of $NH_4^+$ ions increases as the temperature increase in Figure 2 since at higher temperature, the diffusion rate of $NH_4^+$ ions will increase. The effects of ammonia nitrogen sorption at different pH ranges are presented in Figure 3. The minimum equilibrium sorption capacity was achieved at lowest pH (pH 2, 0.400 mg/g). It gradually increases until it reaches optimum sorption at pH 7 (0.828 mg/g). Afterwards, one may notice a trend of decreasing in sorption capacity as the pH increases from 8 to 10. At lower pH values (pH 2 to 4), $H^+$ ions in the aqueous solution and $NH_4^+$ ions are both attracted to the fibers which causes a decrease in the amount of ammonia nitrogen being adsorbed. On the contrary, lignin and cellulose chains in the fibres are negatively charged between pH 5 to 7. This promotes sorption with the positively-charged $NH_4^+$ ions through electrostatic attraction forces[13]. As pH increases beyond neutral (i.e. pH 7), the state of equilibrium sorption shifts rapidly towards the non-ionised form, making it less favourable for ammonia nitrogen removal[15].

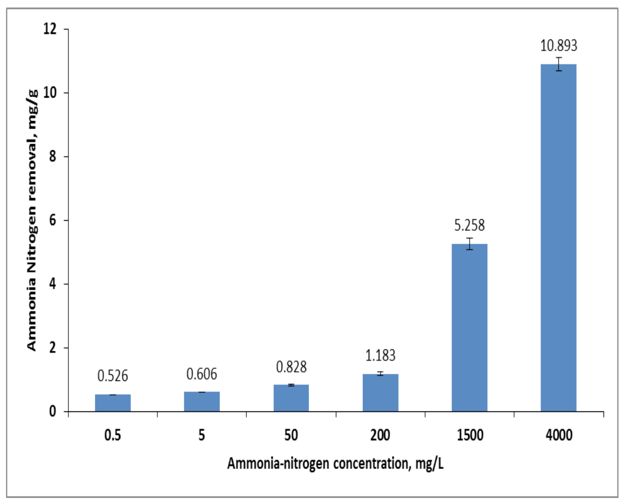


**Figure 1.** Effect of ammonia nitrogen initial concentrations during sorption onto modified EFB (Weight of modified EFB: 15.71 grams, volume of ammonia nitrogen: 1000 mL, contact time: 40 min, room temperature: 27 ± 0.2 $^0$C and pH: 7.0).

The FTIR analysis Figure 4 is used to identify the functional groups involved in ammonia nitrogen sorption onto EFB fibers. As shown in Figure 4, the modified EFB shows peaks shift of C-H methyl and methylene groups from 2918 (unmodified EFB) to 2889 $cm^{-1}$, and $-OCH_3$ from 1029 to 984 $cm^{-1}$. It is noted that hydroxyl group at 3289 $cm^{-1}$ was no longer detected in the modified EFB. In addition, peak for triple bond stretching was observed at 2324 $cm^{-1}$.

These functional groups (-OH, amine and $-OCH_3$) suggest that EFB fibers were structurally modified. Based on FTIR analysis, ammonia nitrogen sorption onto the modified EFB fiber might be due to ion exchanging of $\mathbf{NH_4^+}$ with $Na^+$ (during the modification of EFB fibers), and followed by chemisorptions between ammonium ions and some functional groups (e.g., O-H, -COOH and $-SO_3$ stretching)[16].

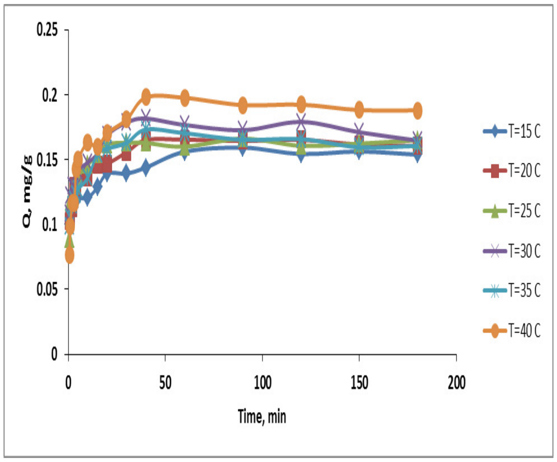


**Figure 2.** Effect of contact time on temperature dependent on sorption capacity of ammonia nitrogen onto the modified empty fruit bunch (Weight of modified EFB: 15.71 grams, ammonia nitrogen concentration: 50 mg/L, and pH: 7.0).

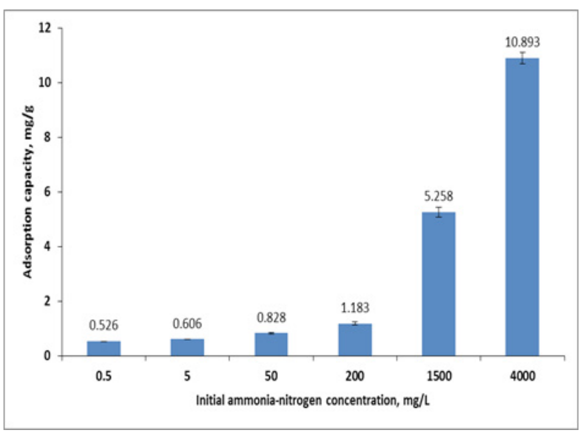


**Figure 3.** Effect of pH on the ammonia nitrogen sorption onto modified empty fruit bunch (Modified EFB fibers weight: 15.71 grams, ammonia nitrogen concentration: 50 mg/L, equilibrium contact time: 40 min, and room temperature: 27 ± 0.2 $^0$C).

## 3.2 Desorption Studies

In order to study the reusability of the adsorbed ammonia nitrogen by EFB fibers, the desorption

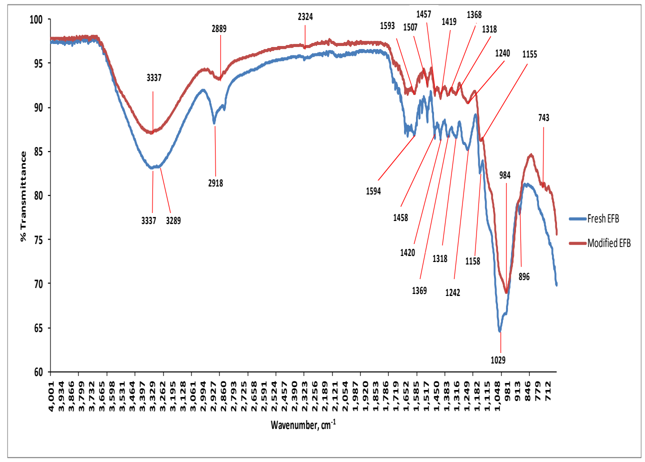


**Figure 4.** FTIR spectra of unmodified and modified empty fruit bunch (EFB) fibers (EFB mass = 0.5 g).

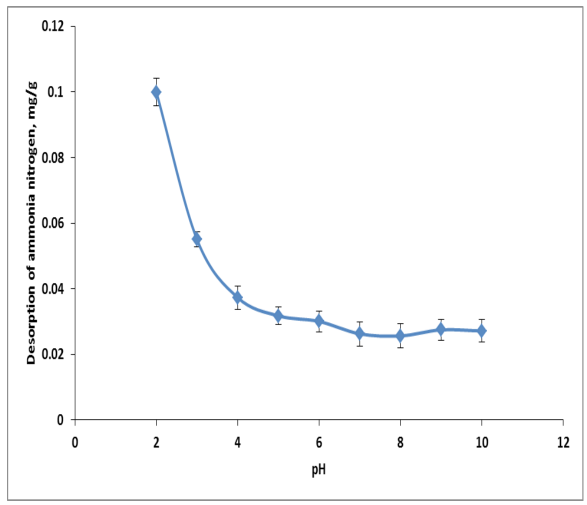


**Figure 5.** Effect of pH on the desorption of ammonia nitrogen from modified empty fruit bunch fibers (Sorption conditions: EFB fibers weight: 15.71 grams, ammonia nitrogen concentration: 50 mg/L, equilibrium time: 40 min and temperature = 27 ± 0.2 $^0$C; desorption conditions: EFB fibers weight: 15.71 grams/L, equilibrium contact time: 40 min and temperature = 27 ± 0.2 $^0$C).

study was carried out by changing the solution pH. The effect of solution pH on the desorption of ammonia nitrogen is displayed in Figure 5. The adsorbed ammonia nitrogen can be desorbed using water due to weak bonding between the fiber and ammonium ion. The maximum ammonia nitrogen recovery from adsorbed EFB fiber was found at pH 2 (0.0999 mg/g) and it gradually decreased to pH 10 (0.0271 mg/g) shown in Figure 5. As the pH increases from 2 to 6, the total ammonia nitrogen desorbed from the EFB surface decreases and it remains nearly constant from pH 6 to 10. The adsorbed ammonium ($NH_4^+$) ions onto the carboxyl group (-RCOO-) of the fibers might be replaced with the hydrogen ($H^+$) ions by ion exchange during the desorption of ammonium at lower pH[17]. The recovered ammonia nitrogen has immense reusability potential which includes soil conditioning[18].

## 4. Conclusions

This study demonstrates the application of modified EFB fibers as adsorbent for the recovery of ammonia nitrogen from aqueous solutions. The ammonia nitrogen from the EFB fiber can be desorbed using an acid solution with maximum desorption capacity of 0.0999 mg/g. The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website[19] and organised by The Center of Excellence for Advanced Research in Fluid Flow (CARIFF)[20]. The publications on products from natural resources, polymer technology, and pharmaceutical technology have been published as a special note in volume 2[21]. The conference host being University Malaysia Pahang[22] is the parent governing body.

## 5. Acknowledgements

Authors would like to thank Universiti Malaysia Sabah (SG10013) for funding this work.

## 6. References

1. Landner L. Sources of nitrogen as a water pollutant: industrial waste water. Progress Water Technology. 1975; 8(4–5):55–65.
2. Zahrim AY, Gilbert ML, Janaun J. Treatment of pulp and paper mill effluent using photo-fenton's process. Journal of Applied Sciences. 2007; 7(15):2164–7. https://doi.org/10.3923/jas.2007.2164.2167
3. Wang L–S, Hu H–Y, Wang C. Effect of ammonia nitrogen and dissolved organic matter fractions on the genotoxicity of wastewater effluent during chlorine disinfection. Environmental Science and Technology. 2007; 41(1):160–5. https://doi.org/10.1021/es0616635
4. Kumar GS, Bharadwaj J, Sruthi PL, Sekhar MC. Removal of ammonia nitrogen (NH4-N) from landfill leachate by chemical treatment. Indian Journal of Science and Technology. 2016; 9(30):1–4.
5. Zahrim AY, Lija Y, Ricky LNS, Azreen I. Fruit waste adsorbent for ammonia nitrogen removal from synthetic solution: Isotherms and kinetics. IOP Conference Series: Earth and Environmental Science. 2016; 36(1):1–6. https://doi.org/10.1088/1755-1315/36/1/012028
6. Demırak A, Keskin F, Şahın Y, Kalemcı V. Removal of ammonium from water by pine cone powder as biosorbent. Mugla Journal of Science and Technology. 2015; 1(1):5–12. https://doi.org/10.22531/muglajsci.209992
7. Badri KH, Juan CA, Hassan O, Mustapha WAW. Analytical approaches of determining monosaccharides from alkaline-treated palm fiber. Malaysian Journal of Analytical Sciences. 2015; 19(1):46–54.
8. Zahrim AY, Ricky LNS, Shahril Y, Rosalam S, Nurmin B, Harun AM, Azreen I. Partly decomposed empty fruit bunch fiber as a potential adsorbent for ammonia-nitrogen from urban drainage water. Springer Singapore; 2015. p. 989–1001. https://doi.org/10.1007/978-981-287-290-6_86
9. Chen Y, Ding L, Fan J. Ammonia-nitrogen sorptional properties of banana peels. Water Environment Research. 2011; 83(4):368–72. https://doi.org/10.2175/106143010X12851009156042 PMid:21553592
10. Ali N, Aziz CAC, Hassan O. Alkali pretreatment and acid hydrolysis of coconut pulp and empty fruit bunch to produce glucose. Jurnal Teknologi. 2015; 74(7):7–11. https://doi.org/10.11113/jt.v74.4687
11. Jeon H, Kang K–E, Jeong J–S, Gong G, Choi J–W, Abimanyu H, Ahn BS, Suh D–J, Choi G–W. Production of anhydrous ethanol using oil palm empty fruit bunch in a pilot plant. Biomass and Bioenergy. 2014; 67:99–107. https://doi.org/10.1016/j.biombioe.2014.04.022
12. HACH. DR/2010 spectrophotometer procedures manual. Spectrophotometer Handbook, U.S.A; 2012.
13. Jellali S, Wahab MA, Anane M, Riahi K, Jedidi N. Biosorption characteristics of ammonium from aqueous solutions onto Posidonia oceanica (L.) fibers. Desalination. 2011; 270(1–3):40–9. https://doi.org/10.1016/j.desal.2010.11.018
14. Liu H, Dong Y, Liu Y, Wang H. Screening of novel low-cost adsorbents from agricultural residues to remove ammonia nitrogen from aqueous solution. Journal of Hazardous Materials. 2010; 178(1–3):1132–6. https://doi.org/10.1016/j.jhazmat.2010.01.117 PMid:20189302
15. Thornton A, Pearce P, Parsons SA. Ammonium removal from digested sludge liquors using ion exchange. Water Research. 2007; 41(2):433–9. https://doi.org/10.1016/j.watres.2006.10.021 PMid:17161445
16. Sharifnia S, Khadivi MA, Shojaeimehr T, Shavisi Y. Characterization, isotherm and kinetic studies for ammonium ion adsorption by Light Expanded Clay Aggregate (LECA). Journal of Saudi Chemical Society. 2012; 20(S1):S342–51.

17. Ma Z, Li Q, Yue Q, Gao B, Li W, Xu X, Zhong Q. Adsorption removal of ammonium and phosphate from water by fertilizer controlled release agent prepared from wheat straw. Chemical Engineering Journal. 2011; 171(3):1209–17. https://doi.org/10.1016/j.cej.2011.05.027
18. Zahrim AY, Asis T, Hashim MA, Al-Mizi TMTMA, Ravindra P. A review on the empty fruit bunch composting: Life cycle analysis and the effect of amendment(s). In: Advances in Bioprocess Technology, Springer; 2015. p. 3–15. https://doi.org/10.1007/978-3-319-17915-5_1
19. FluidChe 2017 Available from: http://fluidsche.ump.edu.my/index.php/en/
20. The Center of Excellence for Advanced Research in Fluid Flow (CARIFF) Available from: http://cariff.ump.edu.my/
21. Natural resources products prospects - International Conference on Fluids and Chemical Engineering FluidsChE 2017 Malaysia, ). Indian Journal of science and technology. 2017; S2(1).
22. University Malaysia Pahang. Available from: www.ump.edu.my