International Journal of Integrated Engineering, Vol. 10 No. 8 (2018) p. 27-32
© Penerbit UTHM
DOI: https://doi.org/10.30880/ijie.2018.10.08.009

Utilization of Empty Fruit Bunch Fibre as Potential Adsorbent for Ammonia Nitrogen Removal in Natural Rubber Wastewater

Nazlizan Nasir[1], Zawawi Daud[1*], Halizah Awang[2], Nur Adila Ab Aziz[1], Baharin Ahmad[1], Mohd Baharudin Ridzuan[1], Mahmoud Hijab Abubakar[1], Husnul Azan Tajarudin[3]

[1]Centre of Advance Research for Integrated Solid Waste Management (CARISMA), Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400, Johor Malaysia
[2]Faculty of Technical and Vocational Education, Universiti Tun Hussein Onn Malaysia, 86400, Johor, Malaysia.
[3]Bioprocess Technology Division, School of Industrial Technology, Universiti Sains Malaysia, Gelugor 11800, Malaysia.

Received 28 October 2018; accepted 11 December 2018, available online 29 December 2018

Abstract: The objective of this study was to identify the performance of empty fruit bunch (EFB) to assess its use as potential adsorbent in treat ammonia nitrogen in natural rubber wastewater. The adsorption method was employed to investigate the effect of a number of factors, namely, adsorbent dosage, pH, shaking speed and contact time. The results revealed that the removal of ammonia nitrogen up to 79.5% from natural rubber wastewater. The adsorption efficiency of EFB fibre was maximum at 3.5 g dosage, pH 7, 150 rpm shaking speed and 120 min contact time. The results proved that EFB fiber are good alternative low cost adsorbent for the removal of ammonia nitrogen from natural rubber wastewater. The Langmuir isotherm (R^2=0.9923) described ammonia nitrogen adsorption slightly better than the Freundlich isotherm (R^2 = 0.9450), suggesting a monolayer adsorption behaviour of the adsorption processes.

Keywords: Wastewater, natural rubber, EFB, ammonia nitrogen, adsorption

1. Introduction

Industrial wastewaters are played one of the most important roles in environmental pollutions, but discharge these wastewater to environment has always with irreparable damages. Today, for the treatment of these pollutants and its control, various methods have been developed. Rubber industrials are among industrials that are highly contaminated effluent and need special consideration in their treatment [1]. Rubber wastewater contribute to suspended solids (SS), dissolved solids, high biochemical oxygen demand (BOD), colour, chemical oxygen demand (COD), and ammonia nitrogen other soluble substances [2]. These highly contaminated water has a high environmental impact and therefore needs to be treated before being discharged to the environment [3,4].

Generally, the technologies of wastewater treatment of natural rubber processing are based on conventional biological processes, such as oxidation ditch, pond system, activated sludge and anaerobic digestion [5]. Though, these systems are ineffective for the degradation of recalcitrant organics and micro-pollutants in rubber wastewater. In addition, these systems need large treatment area and need a long retention times. Physical and chemical methods like coagulation–flocculation, ultrasonic irradiation, ozonation and electrochemical methods have been applied. Nevertheless, these methods have some operational problems like sludge generation, reaction rates and low efficiencies, high operative costs and phase change of pollutants [6].

Adsorption processes using activated carbons are widely used to remove pollutants from wastewaters but the high cost of activated carbon makes its use limited [7–10]. This encourages researchers to find a low-cost adsorbed materials, One of them is empty palm oil bunches or EFB. EFB fibre are easily available in Malaysia so the present study was designed to exploit these abundantly available agricultural wastes for the treatment of natural rubber wastewater to remove ammonia nitrogen from wastewater. The study were also conducted to optimize process parameters like adsorbent dosage, pH, shaking speed and contact time. Meanwhile, the adsorption data of ammonia nitrogen were further analysed using the two commonly used models, namely Langmuir and Freundlich models.

2. Materials

Empty fruit bunch fibre was obtained from Palm Oil factory located at Kluang, Johor state of Malaysia. Then EFB fibre was modified with citric acid according to

*Corresponding author: zawawi@uthm.edu.my

Sajab et al. [11]. 10 g of EFB fibres was added to 100 ml of 0.6M CA at room temperature. The liquid was decanted and the wet fibres were dried in an oven at 50°C for 24 h. The temperature of the oven was raised to 120 °C and maintained at this temperature for 90 min. The modified EFB fibres were washed with hot water to remove excess CA. The fibres were then dried in the oven at 50 °C for 24 h and stored in a desiccator. The chemical composition of EFB fibers such as cellulose, hemicelluloses and lignin were determined by using the following respective standard methods: T 222 om-06, Chlorination and Kurschner-Hoffner Methods [12].

2.1 Wastewater

Natural rubber wastewater was collected from discharge point of a plant located in natural rubber factory at Kluang, Johor, Malaysia. The samples immediately transferred to the laboratory before being preserved in a refrigerator at a temperature of below 4 °C to avoid further biodegradation. The characteristic of wastewater were analysed according to the Standard Methods for Examination of Water and Wastewaters [13].

2.2 Batch Experiment

Optimization of important process parameters such as adsorbent dose, pH, shaking speed and contact time for the maximum removal of colour from natural rubber wastewater was carried out by using classical approach. The 250-mL conical flasks containing 100 mL of natural rubber wastewater with known adsorbent dose were shaken in orbital shaker at 150 rpm in 90 min contact time.

2.3 Adsorption Study

Batch experiments were conducted using the batch method to determine the range of the process variable which includes dosage, pH, shaking speed and contact time. Each of the process variables for those need optimized was investigated and monitored separately. Experiment performed by using EFB fibre as a media and 100mL of wastewater in a 250mL erlenmeyer flask. The flask lid was wrapped with laboratory film (Parafilm M, USA) for ensure satisfactory agitating process. The prepared flask was agitated with orbital shaker (Sartorius, Germany). Then the flask was removed and allowed to settle a bit before the supernatant was withdrawn for analysis of ammonia nitrogen [14]. The adsorption data of ammonia nitrogen by EFB were further analysed using the two commonly used models, namely Langmuir and Freundlich models to ascertain the favourability of the adsorbent.

3. Results and Discussion

3.1 Characterization of Adsorbent

Table 1 show the EFB constitutes a lignocellulose material which consists of chemical component of 52% cellulose, 27% hemicellulose, 17.5% lignin and 3.4 ashes. Oil palm biomass is lignocellulose residues composed of cellulose, hemicellulose, lignin and ash [15]. The present high of cellulose is important; it contribute to the better adsorption of oil, heavy metal and other pollutant [16]. Besides that, functional groups present in lignocellulose materials bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [17]. According to Wong et al., [18], that cellulose, hemicelluloses, and lignin contains a large number of hydroxyl groups. Hydroxyl groups play as an important groups in absorbent and adsorbent process.

Table 1. Chemical composition of oil palm empty fruit bunches

Properties	EFB fibre
Cellulose (%)	52
Hemicellulose (%)	27
Lignin (%)	17.5
Ash (%)	3.4

3.2 Characteristic of Wastewater

Table 2 shows the natural rubber wastewater characteristic used in this study. This study is focused on only four parameters, namely suspended solids (SS), colour, COD and ammonia nitrogen. Table 1 show the presence of ammonia nitrogen 40 to 70 mg/L and these values are high when compared to Department of Environment Malaysia; Environmental Quality (Industrial Effluents) Regulations 2009 under standard A and standard B [19]. The presence nitrogen component consist mainly of ammonia nitrogen in wastewater as a result of the use of ammonia in the preservation of the latex [20]. It is extremely harmful due to the high toxicity of free ammonia at a pH higher than 8 and the high level of NH_4^+ and other plant nutrients makes it a good medium for algal growth, thus resulting in the eutrophication of water bodies [20].

Table 2. Characteristics of natural rubber wastewater

Characteristics	Unit	Value
Biological Oxygen Demand (BOD)	mg/L	3350
Chemical Oxygen Demand (COD)	mg/L	5260
Total Suspended Solids	mg/L	500
Ammoniacal Nitrogen	mg/L	55
Color	Pt.Co	345
Turbidity	NTU	130
Zinc	mg/L	0.266
Iron	mg/L	0.08
Cu	mg/L	0.05
pH		9.3

3.3 Adsorption Study

3.3.1 Effect of Adsorbent Dosage

The effect of adsorbents dose on the ammonia nitrogen percentage removal for different dosage EFB is presented in Fig.1. As can be seen, removal of ammonia nitrogen increased with increasing EFB dosage content until it reached a maximum value at 69.8%. Increasing adsorbent dosage above optimum dosage had a negligible effect on the increase in removal efficiency of NH4+ ions. This may be attributed to the formation of aggregates at higher solid/liquid ratios or to precipitation of particles [21]. According to Kehinde & Aziz [22], the pattern of removal with dosage of adsorbent media may be due to higher chances of collision between the pollutants and adsorbent (as treatment media are increased) and the availability of more surfaces with sites for adsorption; in which case the adsorption may be physical and controlled by diffusion.

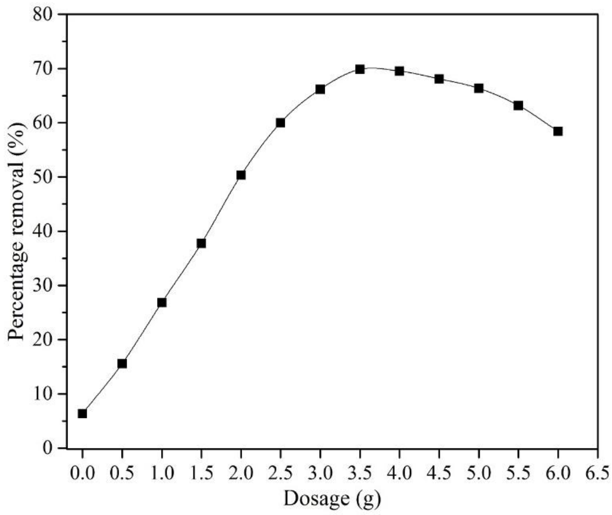

Fig. 1 Effect of EFB on adsorption of ammonia nitrogen

3.3.2 Effect of pH

Ammonia nitrogen removal by EFB was observed at pH values ranging between 3 and 12. The results are depicted in Fig. 2. The figure shows that as solution pH increases in the range of 3 to 6, the removal efficiency of NH_4^+ ion increases gradually and reaches a maximum value 67.9% using EFB when the pH value is 7. When the pH increases to 8, the removal efficiency start to decrease for these adsorbent. This finding tallies with the observations reported by previous authors [23,24]. Explained by Halim *et al.,* [25], the properties of ammonia nitrogen in aqueous solution explain the result; the existence of two types of elements, ammonia, NH_3 (basic) and ammonium ions, NH_4^+ (acidic). Therefore, the removal of ammonia is supposed to be higher at low pH, and vice versa, due to the cation exchange mechanism in aqueous solution.

Meanwhile, according to Huang et al., [23], this behaviour can be explained by the fact that at pH values above 8 partial dissolutions of the adsorbent occurs, and it is also likely that NH_4^+ is converted into NH_3 specimen. Though, at pH values below 8, the NH_4^+ ion concentration in solution rises when pH decreases there nevertheless results a decline in removal efficiency, as the H^+ ion concentration also increases with the decrease in pH and intensifies competition for exchanging sites. Thus, the optimum pH value that suitable to be used for the experiments was pH 7.

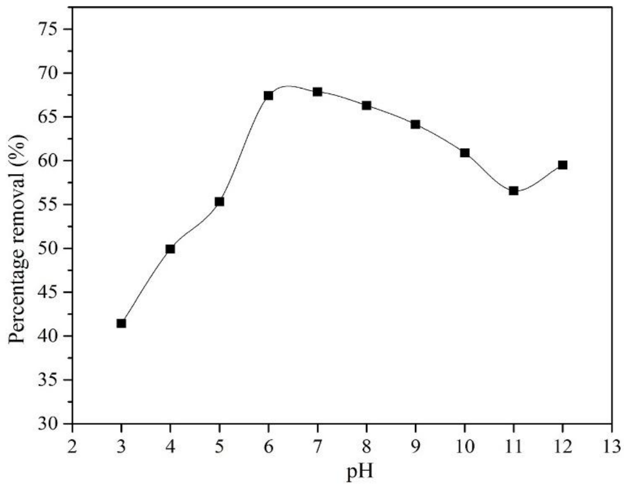

Fig. 2 Effect of pH on adsorption of ammonia nitrogen

3.3.3 Effect of Shaking Speed

Fig. 3 shows the effect of shaking speed results towards the removal of ammonia nitrogen from natural rubber wastewater, a specific range of shaking speed was assigned in the range of 50 to 175 rpm. As can be seen, the removal efficiency of ammonia nitrogen increase when shaking speed increases. According to Salman *et al.*, [26], at very slow agitation speed the adsorbent accumulates at the bottom, reducing the contact surface area of the adsorbent with the adsorbate.

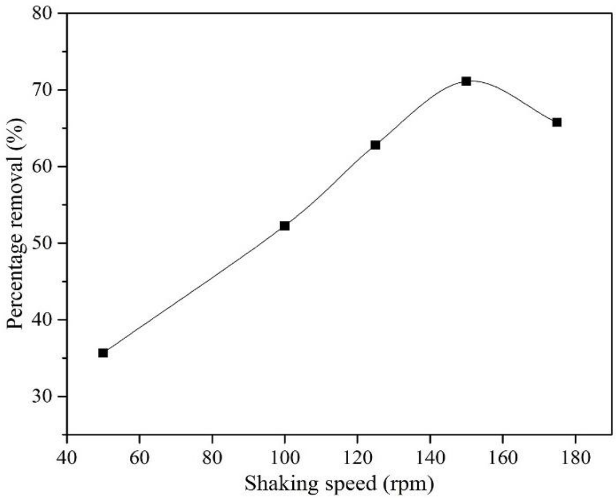

Fig. 3 Effect of shaking speed on adsorption of ammonia nitrogen

Meanwhile, by increasing the shaking speed, there is a further raised in the adsorption due to the binding sites are free for further adsorption. With shaking, the external mass transfer coefficient raises causing the faster adsorption of the ammonia nitrogen [8]. Moreover, at very high speed, centrifugal forces operate, resulting in desorption of the adsorbate [21]. The optimum shaking speed obtained from experiment was 150 rpm with the removal efficiency of 71.1%, using EFB. Once reached the equilibrium state, if the shaking speed continued to increase, the removal rate tends to remain constant. Thus, agitation 150 rpm show the most suitable for this study.

3.3.4 Effect of Contact Time

The effect of contact time on the absorption of ammonia nitrogen on empty fruit bunch was shown in Fig. 4. The result showed that the ammonia nitrogen was rapidly adsorbed in the first 60 min with the increase of contact time from 0-60 min and the ammonia nitrogen removal increased to 79.5% using EFB within 120 min. After 120 min, the adsorption rate becomes constant and the adsorption reach equilibrium. The maximum of ammonia nitrogen removal ammonia nitrogen removal was 79.5% using EFB at contact time 120 min.

According to Auta & Hameed, [27], fast ammonia nitrogen adsorption at initial stage with respect to the contact time and gradually became slower as equilibrium position was approached. Numerous and vacant active surface sites of the adsorbents were available at the initial stage of the reaction, and as the time lapsed, the vacant sites reduced in number thereby slowing down the adsorption process.

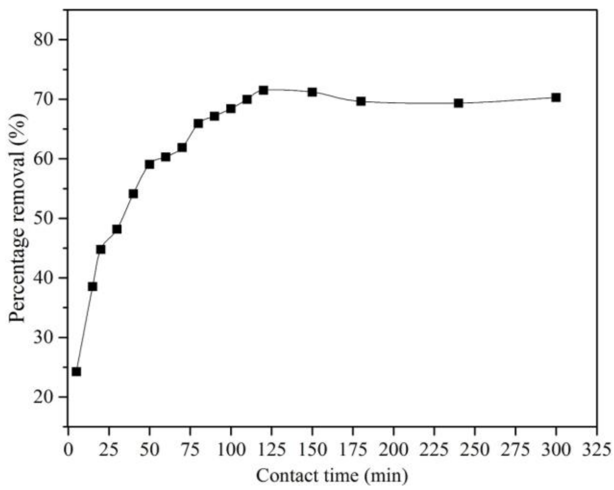

Fig. 4 Effect of contact time on adsorption of ammonia nitrogen

3.4 Adsorption Isotherm

Isotherm study is a basic technique for determining the nature of adsorption between the adsorbent and ammonia nitrogen. It indicates the distribution of ammonia nitrogen in the equilibrium phase. Langmuir and Freundlich are the most commonly used models for evaluating the experimentally acquired adsorption isotherms [28,29,30,31,32,33]. As be seen in Table 3, high R^2 are derived by fitting experimental data into the Langmuir isotherm model for EFB (0.9923) as compared with the Freundlich isotherm model (0.9450). These suggest that Langmuir isotherm model enable generate a satisfactory fit to the experimental data, while Freundlich isotherm model vise versa. This Langmuir model assumes surface containing a limited number of adsorption sites and apply monolayer adsorption with no transmigration of adsorbate in the smooth of surface [21].

Table 3. The adsorption isotherm parameters of ammonia nitrogen adsorption

Isotherm parameter	EFB
Langmuir	
q_m	3.3772
K_L	0.2792
R^2	0.9923
Freundlich	
K_F	0.2795
n	1.2089
R^2	0.9450

4. Summary

From this study, EFB fiber proven as low-cost and environmentally friendly and capable to remove ammonia nitrogen more than 75% from natural rubber wastewater. On the other hand, the adsorption best described by Langmuir isotherm model as the R2 was closed to 1. However, further research is necessary to see the effectiveness of EFB fiber for the removal of other contaminants in natural rubber wastewater such as colour, suspended solids, COD and others.

Acknowledgments

The authors would like to acknowledge the Ministry of Higher Education, Malaysia and Universiti Tun Hussein Onn Malaysia for financial support under Fundamental Research Grant (FRGS) No. 1457 and 1571 and MyBrain15 (MyPhD).

References

[1] Massoudinejad M, Rabori M M and Dehghani M H. Treatment of natural rubber industry wastewater through a combination of physicochemical and ozonation processes *J. Adv. Environ. Heal. Res.* **Vol. 3**. (2015) 242–9.

[2] Rosman N H, Nor Anuar A, Chelliapan S, Md Din M F and Ujang Z. Characteristics and performance of aerobic granular sludge treating rubber wastewater at different hydraulic retention time *Bioresour. Technol.* **161.** (2014)**.** 155–61

[3] Habeeb, S.A., Latiff, A.A.A., Daud, Z. & Ahmad, Z. The start-up of hybrid, anaerobic up-flow sludge

blanket (HUASB) under a range of mesophiclic and thermophilic temperatures. *EnvironmentAsia*, Volume 4(2), (2011), pp. 63-68.

[4] Watari T, Thanh N T, Tsuruoka N, Tanikawa D, Kuroda K, Huong N L, Tan N M, Hai H T, Hatamoto M, Syutsubo K, Fukuda M and Yamaguchi T. Development of a BR–UASB–DHS system for natural rubber processing wastewater treatment *Environ. Technol.* **37.** (2016) 459–65.

[5] Daud, Z., Nasir, N., Aziz Abdul Latiff, A., Ridzuan, M.B. & Awang, H. Treatment of biodiesel wastewater by coagulation-flocculation process using polyaluminium chloride (PAC) and polyelectrolyte anionic. *ARPN Journal of Engineering and Applied Sciences*, Volume 11(20), (2016), pp. 11855-11859.

[6] Nguyen N H and Luong T. Situation of wastewater treatment of natural rubber latex processing in the Southeastern region, Vietnam *J. Vietnamese Environ.* **2.** (2012)**.** 58–64.

[7] Bhatti H N, Sadaf S and Aleem A.Treatment of textile effluents by low cost agricultural waste: Batch biosorption study *J. Anim. Plant Sci.* **25.** (2015). 284–9.

[8] Adeleke A O, Latiff A A A, Al-Gheethi A A and Daud Z. Optimization of operating paramters of novel composite adsorbent for organic pollutant removal from POME using response surface methodology *Chemosphere* **174.** (2017) 232–242.

[9] Daud, Z., Abubakar, M.H., Kadir, A.A., Latiff, A.A., Awang, H., Halim, A.A., Marto, A., Optimization of leachate treatment with granular biomedia: Feldspar and Zeolite. *Indian Journal of Science and Technology*, Volume 9(37), (2016), 91845.

[10] Latiff, A. A. A., Adeleke Abdul Rahman, O., Daud, Z., Ridzuan, M. B., & Mat Daud, N. F., Batch Adsorption of Manganese from Palm Oil Mill Effluent Onto Activated Cow Bone Powder. *ARPN Journal of Engineering and Applied Sciences*, Volume 11(4), (2016), pp. 2627-2631.

[11] Sajab M S, Chia C H, Zakaria S and Khiew P S. Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions *Bioresour. Technol.* **128** (2013). 71–75.

[12] Daud, Z., Hatta, M.Z.M., Kassim, A.S.M., Awang, H., Aripin, A.M., Exploring of agro waste (pineapple leaf, corn stalk, and napier grass) by chemical composition and morphological study. *BioResources*, Volume 9 (1), (2014), pp. 872-880.

[13] APHA 2012 Standard Methods for the Examination of Water and Wastewater 2012.

[14] Nasir, N. and Daud, Z., Performance of Aluminium Sulphate and Polyaluminium Choloride In Biodiesel Wastewater. *Journal of Mechanical Engineering and Sciences*, Volume 7(1), (2014), pp. 1189-1195.

[15] Khalil H P S A, Jawaid M, Hassan a, Paridah M T and Zaidon. Oil Palm Biomass Fibres and Recent Advancement in Oil Palm Biomass Fibres Based Hybrid Biocomposites *Compos. Their Appl.* (2012), 187–220.

[16] Kudaligama K V V S, Thurul W M and Yapa P A J. A Cost Effective Solution for Treatment of *J. Rubber Res.* **13** (2010). 18–26

[17] Vakili M, Rafatullah M, Salamatinia B, Zuhairi A, Hakimi M, Bing K, Gholami Z and Amouzgar P. Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater : A review *Carbohydr. Polym.* **113** (2014). 15–30.

[18] Wong Y C, Senan M S R and Atiqah N A. Removal of Methylene Blue and Malachite Green Dye Using Different Form of Coconut Fibre as Absorbent *J. Basic Appl. Sci.* **9** (2013) 172–7.

[19] Mokhtar N M, Lau W J, Ismail A F and Veerasamy D.Membrane Distillation Technology for Treatment of Wastewater from Rubber Industry in Malaysia *Procedia CIRP* **26** (2015). 792–796.

[20] Pillai H P J S and Girish K. Original Research Article Rubber processing industry effluent treatment using a bacterial consortium *Int. J. Curr. Microbiol. Appl. Sci.* **3** (2014). 775–782.

[21] Daud, Z., Abubakar, M.H., Kadir, A.A., Latiff, A.A.A., Awang, H., Halim, A.A. & Marto, A., Adsorption studies of leachate on cockle shells. *International Journal of GEOMATE*, Volume 12(29), (2017), pp. 2186-2990.

[22] Kehinde F. and Aziz H A. Journal of Environmental Chemical Engineering Classical optimization of process variables in the treatment of real textile wastewater using clinoptilolite *Biochem. Pharmacol.* (2015). 6–11.

[23] Huang H, Xiao X, Yan B and Yang L. Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent *J. Hazard. Mater.* **175** (2010) 247–252.

[24] Kamaruddin M A, Yusoff M S, Aziz H A and Alrozi R. Preparation and Characterization of Activated Carbon Embedded Clinoptilolite Adsorbent for Colour Removal from Textile Effluent *J. Mater. Chem. Eng.* **2** (2014) 1–10.

[25] Halim A, Abidin N, Awang N, Ithnin A, Othman M and Wahab M. Ammonia and cod removal from synthetic leachate using rice husk composite adsorbent *J. Urban Environ. Eng.* **5** (2011). 24–31.

[26] Salman M, Athar M, Shafique U, Rehman R, Ameer S, Ali S Z and Azeem M. Removal of formaldehyde from aqueous solution by adsorption on kaolin and bentonite: A comparative study *Turkish J. Eng. Environ. Sci.* **36** (2012) 63–70

[27] Auta M and Hameed B H. Chitosan – clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue *Chem. Eng. J.* **237** (2014). 352–61.

[28] Abdulrahman, A., Latiff, A.A.A., Daud, Z., Ridzuan, M.B., Jagaba, A.H., Preparation and Characterization of Activated Cow Bone Powder for the Adsorption of Cadmium from Palm Oil

Mill Effluent. *IOP Conference Series: Materials Science and Engineering*, Volume 136 (1), (2016), 012045.

[29] Adeleke, A. R. O., Abdul Latiff, A. A., Daud, Z., Ridzuan, B., and Mat Daud, N. F., Remediation of Raw Wastewater of Palm Oil Mill Using Activated Cow Bone Powder through Batch Adsorption. *Key Engineering Materials*, 705, (2016), pp. 380-384.

[30] Balakrishnan, B., Awal, A.S.M.A., Abdullah, A.B., Hossain, M.Z. Flow properties and strength behaviour of masonry mortar incorporating high volume fly ash. *International Journal of GEOMATE*, Volume 12 (31), (2017), pp. 121-126.

[31] Al-Gheethi, A.A., Mohamed, R.M.S.R., Efaq, A.N., Norli, I., Halid, A.A., Amir, H.K., Kadir, M.O.A. Bioaugmentation process of secondary effluents for reduction of pathogens, heavy metals and antibiotics. *Journal of Water and Health*, Volume 14 (5), (2016), pp. 780-795.

[32] Sohu, S., Abd Halid, A., Nagapan, S., Fattah, A., Latif, I., Ullah, K. Causative factors of cost overrun in highway projects of Sindh province of Pakistan. IOP Conference Series: Materials Science and Engineering, Volume 271 (1), (2017), art. no. 012036.

[33] Wang, F., Abdullah, A.H. Investigating thermal conditions in a tropic atrium employing CFD and DTM techniques. *International Journal of Low-Carbon Technologies*, Volume 6 (3), (2011), art. no. ctr005, pp. 171-186.