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A STUDY ON COMBINATION OF BIOCHAR AND ACTIVATED SLUDGE FOR REMOVING AMMONIUM FROM LOW C/N RATIO WASTEWATER

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Abstract. Grey domestic wastewater from septic tank contains high nitrogen content especially ammonium and low C/N ratio. Therefore, the aerobic biological treatment is often not effective for ammonium and nitrogen removal. The aim of this work was to study the performance of ammonium removal and production of aerobic granular sludge using biochar produced from coffee husk pyrolyzed at 350 ^oC as biocarrier. It was performed under the lab-scale SBR systems. Low C/N ratio domestic wastewater was used for this work. Coffee husk biochar (CFH 350) was added into the systems at different dosage. As a result, the biochar made from coffee husk pyrolyzed at low temperature promoted the adhesion of microbial sludge onto biochar surface. The particles size of biochar played an important role for adhesion of microbial sludge on biochar. The growth rate of bacterial sludge was accelerated and higher than control sample when biochar was used with biochar dose of 15 g/L. Though nitrification rate was improved as the microbial sludge was accelerated, however, at initial stage, the removal efficiency of COD and ammonium was not as high as compared to traditional activated aerobic sludge system.

Keywords: biochar, ammonium, aerobic granular sludge, wastewater.

Classification numbers: 3.3.1, 3.3.2, 3.3.3.

1. INTRODUCTION

Ammonium released from municipal, industrial and agricultural activities can cause serious issues to receiving waters, such as accelerating eutrophication, depleting dissolved oxygen, and harming aquatic organisms. Biologically, ammonium removal using several processes, such as membrane reactors, anaerobic ammonium oxidation, sequential combined aerobic and anaerobic batch reactors, nitrification followed by denitrification in constructed wetlands have received reasonable research attention [1, 2]. Likewise, adsorption methods with activated carbons, or with zeolites for ammonia removal have been widely explored [3, 4]. Among those methods, physical removal method using low-cost adsorbents is the most competitive ways for the removal of ammonium from piggery manure slurry because of its performance and cost.

So far, Powdered Activated Carbon Treatment (PACT) has been used in wastewater technology. PACT could be added directly into the anaerobic or aerobic tanks. As a result, the

PACT could adsorb some recalcitrant compounds in the system. However, PACT would be affected strongly by several factors in the reactor, such as microbial sludge concentrations, retention time. In addition, PACT would cause a high-cost wastewater treatment. Recently, biochar is a pyrogenic carbon material that has attracted much attention. Biochar derived from agricultural wastes such as straw, bagasse, and animal manure can be used as a low-cost adsorbent for the removal of contaminants such as heavy metals, ammonium, and organic pollutants from water [5, 6]. Recently, much attention has been focused on the application of biomass resources for biochar production via various pyrolysis processes at relatively low temperatures (lower than 700 °C) as low-cost adsorbent [7]. The conversion of waste materials into biochar is beneficial as it adds up considerable economic value; waste disposal cost reduction and it could be an alternative choice for adsorbent demand. Biochars produced from different feed materials showed various adsorptive capacity resulting from variations in surface chemistry [8]. However, biochars especially biochar derived from agriculture wastes were only applied in restricted fields due to its limited functionalities, inherited from the feedstock after slow pyrolysis process [9]. Raw or un-activated biomass biochar usually showed relatively lower pore properties and therefore have limited ability to adsorb various contaminants, particularly for high concentrations of polluted water and wastewater. So far, there has been a growing interest of research on physical and chemical activation of biochar for improving its chemical/physical properties in order to widen its application in the past few years [9, 10]. Biochar exhibits varying degrees of adsorptive capacity for pesticides, explosives, polyaromatic hydrocarbons, radionuclides, heavy metals, ammonium, nitrate, phosphate, or other groundwater contaminants [11, 12]. Some biomass-derived biochars were potentially effective bio-adsorbents for C and N in water and wastewater treatment [5, 13], however so far little information about research of applying coffee husk biochar in activated sludge system for C and nitrogen removal. Moreover, microbial communities and their attachment in biochar had not been examined, especially with respect to biochar properties (e.g., pH, particle size, solid/ liquid ratio etc.). It should be noted that grey water discharged from septic tank contains high nitrogen content and low C/N ratio, so that the aerobic biological treatment may not be effective for nitrogen removal.

This study, therefore, aimed to investigate the application of biochar from agricultural wastes to remove the excess nitrogen in domestic wastewater. In particular, this work examined the utilization of biochar obtained from coffee husk pyrolyzed at 350 ^{o}C to adsorb ammonium. Besides, adding biochar could be a simple and effective method for the initiation of activated sludge granulation to facilitate the treatment of low C/N ratio wastewater. In this work, ammonium removals by both biochar (as adsorption process) for initial stage; and microbial sludge (as nitrification/denitrification process) were evaluated in details.

2. MATERIALS AND METHODS

2.1. Preparation of biochar

In this experiment, biochar was obtained through the pyrolysis of coffee husk at 350 ^{o}C. The coffee husk was washed several times with distilled water to remove adhering impurities. The sample was dried at 105 ^{o}C until reach the constant weight. Later about 50 g of dried sample was ground and sieved to yield a uniform 2 mm size fraction and was put into a porcelain crucible covered with a lid. The crucible was placed in a muffle furnace (Lenton Thermal) with heating rate of 15 ^{o}C/min and pyrolyzed at 350 ^{o}C for 1 hr under a limited-oxygen condition. Biochar after being collected was washed, oven-dried at 105 ^{o}C and screened to obtain different particles sizes. Finally, it was stored in a plastic bottle and put in a desiccant cabinet for use as the adsorbent. Biochar later was determined of some properties such as moisture, ash content, the pH value at the point of zero charge (pH_{pzc}), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM). Biochar was marked as CFH 350 for further experiments.

2.2. Activated sludge preparation

Activated sludge was taken from an sequencing batch reactor (SBR) of the Yen So WasteWater Treatment Plant (Ha Noi). Later, the sludge was activated and cultured in synthetic wastewater for 1 week in an SBR set up. The synthetic wastewater was prepared by following components: glucose of 1000 mg/L; $NaHCO_3$ 400 mg/L; NH_4Cl - 190 mg/L; K_2HPO_4 - 80 mg/L; $CaCl_2.2H_2O$ - 45 mg/L; $MgSO_4.7H_2O$ - 12 mg/L; $FeCl_3$ of 3.6 mg/L. Trace elements (TE) (1 mL/L) were: H_3BO_3 of 0.15 g/L; $CoCl_2.6H_2O$ - 0.15 g/L; $CuSO_4.5H_2O$ - 0.03 g/L; $FeCl_3.6H_2O$ - 1.5 g/L; $MnCl_2.2H_2O$ - 0.12 g/L; $Na_2Mo_4O_{24}.2H_2O$ - 0.06 g/L; $ZnSO_4.7H_2O$ - 0.12g/L; KI - 0.03 g/L [14]. Activated sludge later was centrifuged at 6000 rpm, for 15 minutes to separate water. The centrifuged sludge was washed 2-3 times and resuspended using pasteurized 0.85 % NaCl. This sludge was stored and used in several experiments to determine the adsorption capacity of biochar for activated sludge. The viable cell count of this sludge was determined by dilution plating method onto nutrient agar plates for counting colony forming units (CFU). Plate count agar (PCA) is a bacteriological substrate used for determination of the total number of live, aerobic bacteria in a sample. The number of bacteria is expressed as colony forming units per ml (CFU/ml). The samples were diluted, and appropriate dilutions were added in Petri plates. Composition of Plate Count Agar: Enzymatic Digest of Casein: 5.0 g/L; Yeast Extract: 2.5 g/L; Glucose 1.0 g/L; Agar: 15.0 g/L. Adjust final pH 7.0 ± 0.2 at 25 °C. The plates are incubated at 30 °C in two days. After incubation, the number of colonies was counted on the plate. The viable cell counts of bacterial for this seed sludge was 2.76×10^6 CFU/mL.

2.3. Experimental procedures

50 mL conical flask containing 10 mL of 0.85 % NaCl cell suspension was incubated by shaking at 30 ^oC for 6 hrs, 12 hrs, 24 hrs and 48 h with 0.5 g CFH 350 (particles size of biochar was 0.2 - 1 mm). Aliquots (0.1 mL) of cell biochar suspension were serially diluted, inoculated onto nutrient agar plates and incubated at 30 ^oC for 48 hrs to examine the effect of different inoculation time on bacterial adsorption on biochar. In all experiments, the cell numbers were determined by PCA method and the number of adsorbed bacterial sludge cell in biochar samples was calculated by subtracting the number of bacteria remaining after adsorption from the initial number of bacteria in suspension. All experiments were conducted with three replicates. 10 mL of seed activated sludge was grown in 100 mL of synthetic wastewater with 0.5; 1 and 0.15 g of CFH 350 accordingly, at 30 ^oC; 130 rpm for 48 hrs. Dilution method was applied for counting bacteria at different time of intervals. Activated sludge was also grown in synthetic wastewater without biochar as control sample. Aliquots (0.1 mL) of cell- biochar suspension were serially diluted, inoculated onto Nutrient Agar (NA) plates and incubated at 30 ^oC for 48 hrs to determine the effect of biochar dose on bacterial growth curve. 250 mL flask containing 100 mL of 0.85 % NaCl cell suspension was incubated with 0.5 g biochar of different particle sizes (lower than 0.2 mm; 0.2 - 1.0 mm; 1.0 - 2.0 mm) by shaking at 30 ^oC for 24 hrs on a rotary shaker. 50 mL flask containing 10 mL of 0.85 % NaCl cell suspension with sludge concentration approximately 3 g/L was incubated with different biochar dose (5, 10, 15 and 20 g/L) with 0.2 - 1 mm biochar particle size, shaking at 30 ^oC for 24 hrs on a rotary shaker. Aliquots (0.1 mL) of

cell- biochar suspension were serially diluted, inoculated onto NA plates and incubated at 30 ^oC for 48 hrs to investigate the effect of biochar size and biochar dose on bacterial sludge adsorption.

In order to investigate the Chemical Oxygen demand (COD) and ammonium removal efficiency of biochar and activated sludge combination system, three parallel SBRs with effective volumes of 2 L with Height /Dimension ratio of 5/1 were used: System A [Wastewater + CFH 350 (5 g/L)]; System B [Wastewater + CFH 350 (5 g/L) + Activated sludge (3 g/L)]; and System C [Wastewater + Activated sludge (3 g/L)]. SBR was operated with the Aeration time of 6 hrs; Settling time of 50 mins; 5 mins of Filling and 5 mins of Decant phase; Dissolved Oxygen (DO) was maintained 4 mg/L by introduced a fine-bubble porous aerator placed at the bottom of the reactors. Some properties of domestic WW: pH = 6,8; Total Suspended Solids (TSS) = 182 mg/L; COD = 486 mg/L; Total Nitrogen (TN) = 350 mg/L; NH_4^+-N = 260 mg/L; NO_3^--N = 7.8 mg/L; Total Phosphorus (TP) = 33 mg/L. Wastewater exchange ratio was of 60 % volume.

2.4. Analytical methods

In this study, the surface areas and pore size distribution of CFH 350 (0.2-1 mm) were determined by the BET method from N_2 isotherms measured at 75.2 K using BET Micrometrics Gemini VII (Micromeritics, Atlanta, USA). The samples were analyzed by high-resolution SEM in an electron microscope with an acceleration of 30 kV and a theoretical resolution of 1 nm (Kruss, Germany). The Fourier Transform Infrared (FTIR) characteristic peaks of the VCP 350 were determined by an infrared spectroscopy analyzer (Thermo Fisher Scientific, Waltham, USA) to characterize the surface organic functional groups present. Other parameters, such as COD, TN, NH_4^+_N, TP were measured using HACH® digestion vials, using a DR 5000 spectrophotometer (Hach, Germany). In particular, COD was analyzed by the closed reflux, colorimetric method (Method 8000). TN was determined by the persulfate digestion method (Method 10071). NH_4^+_N was determined by Salicylate Method (Method 10023). TP was measured by Acid Persulfate Digestion Method (Method 4500 P-E). TSS measurements were carried out following laboratory procedures according to the Standard Methods (methods 2540D). After each batch experiment, sludge samples were taken out for observation during sedimentation phase from the first time when the system started operating, after 1 week and after 3 weeks. 0.1 mL of sludge was sampled and observed on a microscope to follow the adsorption of sludge on biochar and the formation of granules. The growth of aerobic granules in the reactor was observed under an optical microscope XSZ-21, equipped with a digital camera Moticam 1000. Sample was taken by a pipette. It was dropped to the middle of the glass slide. The glass slide was placed in the microscopic equipment. The coarse and fine adjustments on the microscope was used to bring the sample into the field of focus to see clear the sample then photos were taken. In this study, hydraulic analysis was mainly based on the calculation of hydraulic retention time. It was estimated by the volume of reactor and flowrate. The filling time, aeration time, settling time and decanting time of SBR operation were controlled by setting the timer. The hydraulic retention time of the system was selected after conducting intermittent batch studies at different retention times to evaluate the efficiency of COD and ammonium treatment of the system in order to choose the suitable retention time for effective treatment of pollutants and enhancement of granulation process.

3. RESULTS AND DISCUSSION

3.1. Characteristics of CFH 350

SEM images showed that the surface morphology of CFH 350 was rough and heterogeneous (Fig. 1). SEM micrographs of the morphological revealed a changing in the pore structure of the biochar at different temperatures. Normally, unregular fold structure obtained at low pyrolysis temperature and became regular layer with the increasing temperature (400 to 700˚C) [15]. As seen in Fig. 2, due to thermal destruction of cellulose and lignin in the coffee husk material, the surface of CFH 350 might result in the exposure of some function groups such as aliphatic alkyl (CH_2-), hydroxyl (-OH), carboxyl (-COOH) and carbonyl (C=O) [2, 16].

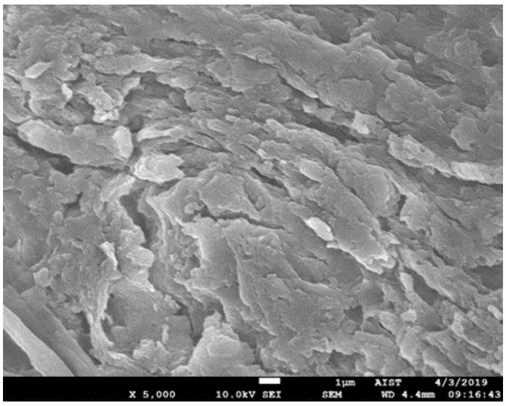

Figure 1. SEM of Biochar CFH 350.

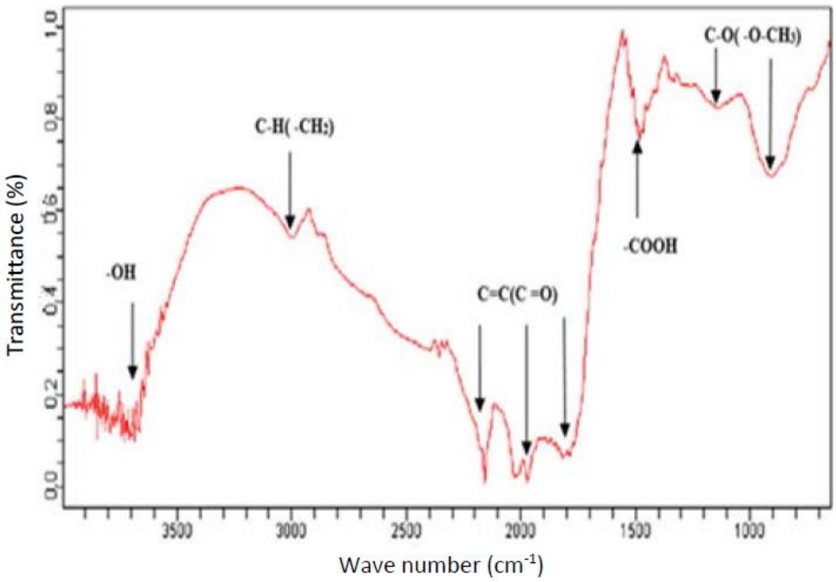

Figure 2. FTIR analysis of biochar CFH 350.

Other research also showed that the carboxyl group and the hydroxyl group and other functional groups on the surface of the carrier can be better combined with the microbial surface, which is beneficial to the rapid immobilization of microorganisms and improve the binding strength between the carrier and the microorganism [17]. BET results showed that the specific surface area and total pore volume of CFH 350 were 0.43 m^2/g and 0.0024 cm^3/g, respectively. The obtained results were relatively low due to the biochar was pyrolyzed at low temperature and had not been activated. BET of biochar was significantly affected by biochar feedstock and pyrolysis temperature [18, 19]. The average pore size of CFH 350 was 2.8 nm. pH_{pzc} of CFH 350 was 7.8, therefore its surface also had a mildly basic character. This pH is common for thermally produced biochars from biomass [20].

3.2. Effect of CFH 350 dose on growth curve of microbial sludge

The effects of biochar dose on the growth of microbial sludge were presented in Fig. 3.

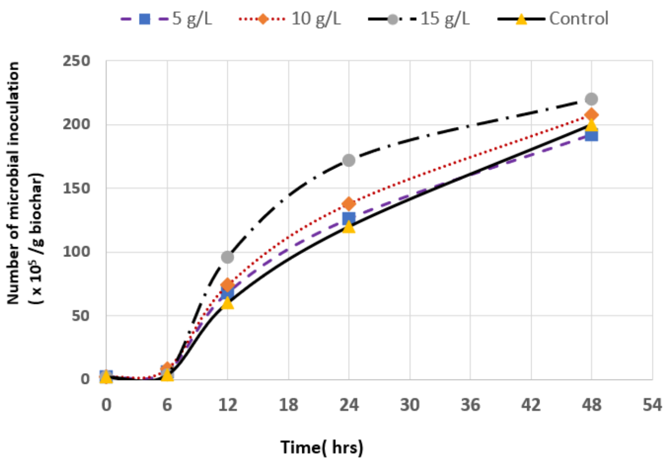

Figure 3. Effect of CFH 350 dose on growth curve of bacterial sludge.

As seen in Fig. 3, the microbial sludge grew fast within the first 24 hrs. The rapid growing was from 6 to 24 hrs in all samples (with or without added biochar). However, there were not much difference when CFH 350 were used with concentration of 5 or 10 g/L. In case of biochar dose of 15 g/L, the growth rate of microbial sludge was accelerated and much higher than control sample. This result indicated that CFH 350 could enhance the growth of microbial sludge in the logarithmic phase due to the retained nutrients on surface of biochar and biochar could be used together with activated sludge in one reactor in order to improve the treatment efficiency. Some recent research indicated that the addition of biochar and activated carbon had no effect on the microbial community of granules and there were likely that biochars accelerated the granulation of activated sludge through physical interactions (affecting the physical characteristic of activated sludge) [17, 21, 22].

3.3. Effect of biochar particles size and biochar dose on microbial sludge adsorption

The effects of biochar particles size and biochar dose on microbial sludge adsorption were shown in Figs. 4a and 4b.

The highest percentage of microbial adsosrption on CFH 350 reached almost 70 % after 24 hrs with biochar particles size ranging from 0.2 - 1.0 mm (Fig. 4a.). Biochar with size of less than 0.2 mm had higher adsorption abilities than biochar with size from 1.0 - 2.0 mm. It could be explained that maybe due to the different surface area of these two sizes of biochar, however the difference was not much significant. Contact area between the biochar and the microbial sludge was, probably one of the most important factors in the adsorption process [21].

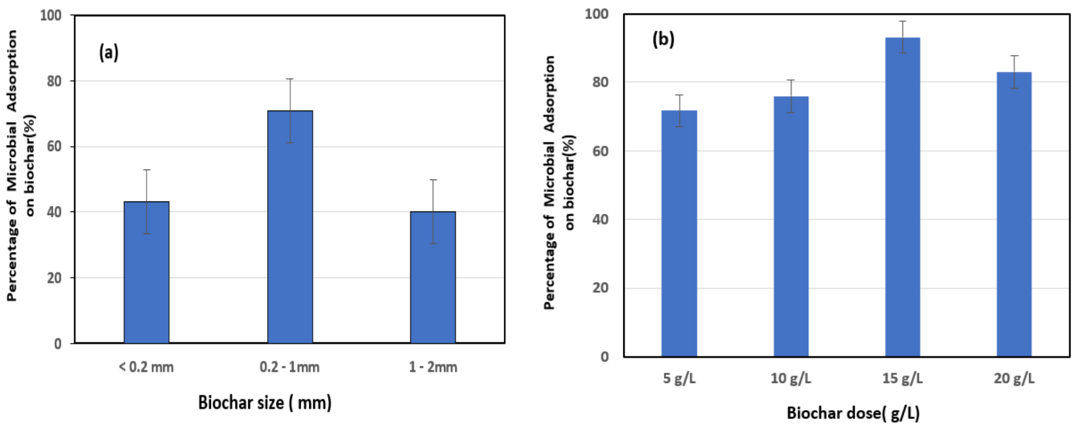

Figure 4. Effect of biochar size (a) and biochar dose (b) on microbial adsorption.

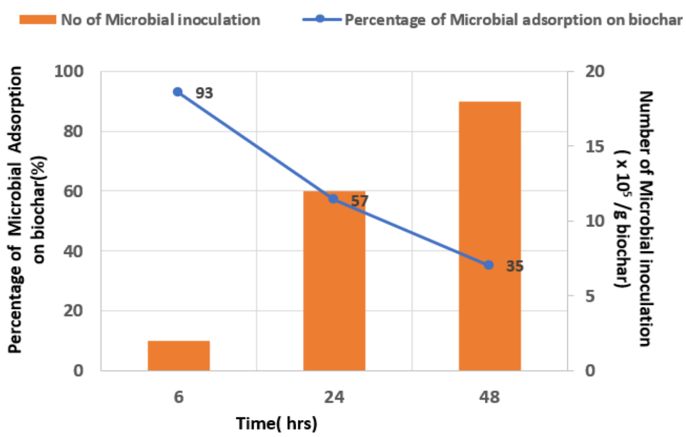

Figure 5. Microbial adsorption under different inoculation time.

As seen in Fig. 4b, the percentage of microbial adsorption on biochar increased when increasing the biochar ratio to reach the highest at biochar dose of 15 g/L (92 %). At ratio of 20 g/L, the adsorption ability was slightly decreased it maybe due to at this concentration, the dispersion of biochar on solution was quite condensed. Over all, the differences in adsorption between different ratios were not noticeably different. The optimal adsorption of microbial sludge onto biochar was obtained with CFH 350 dose of 15 g/L, i.e. equal to the ratio of biochar/activated sludge of 5:1 (w/w).

Microbial adsorption under different inoculation time was presented in Fig. 5. Number of microbial sludge adsorbed onto biochar increased in first 6 hrs of inculation times and reached the highest of 90 %. However, it reduced after 24 hrs to 57 % and 35 % after 48 hrs. It can be seen that microbial sludge in saline solution 0.85 % was attached onto biochar at the first 6 to 24 hrs and seemed to be released into suspension when increased the inoculation time under shaking condition. Recent research determining the best conditions for modified biochar immobilized petroleum hydrocarbon degradation microorganism by orthogonal test showed that modified peanut shell charcoal achieved the highest adsorption rate of bacteria (79 %) after 6 hrs and reduced to 61 % after 24 hrs [23].

3.4. Combination of biochar and activated sludge for COD and ammonium removal

Removal of COD and ammonium by combination of biochar and activated sludge in SBR system was presented in Fig. 6.

As seen in the figure, the removal efficiency of COD and ammonium of SBR system A (only using 5 g/L of CFH 350) was lower than that of system B (CFH 350 (5 g/L) + Activated sludge (3 g/L)) and system C (only activated sludge (3 g/L)). It could be seen that the activated sludge played significant role in the treatment process for COD and ammonium removal in synthetic wastewater. Pollutants were synchronously eliminated with the coupling mechanisms of adsorption onto biochar surface and biodegradation by the related microorganisms. The consortia seemed to be efficient in utilizing carbon and ammonia nitrogen in the simulated wastewater and active biofilm as electron donors during denitrification. In the early stage, when introducing biochar into the aerobic sludge system, the treatment efficiency of this combination system was not much different as compared to the traditional aerobic sludge system. It could be due to that the CFH 350 itself could not achieve the highest removal efficiency of COD or ammonia when the activated sludge was attached on the surface of biochar. As a result, this caused a reduction of adsorption capacity of CFH 350 as mentioned in above. The startup results of combination system were in line with the results reported by Li *et al.* [23]. In the work, after the inoculation period, microorganisms were attached to the biochar and biofilm was slowly developed during the first 10 days. In this period, microorganism could go through self-organization and maturation period, thus the removal rates were not reached of the highest efficiency [24].

After adding CFH 350 into SBR system, microscopic examination showed that in short time (2 - 3 days) microorganisms were tended to be attached and grow onto CFH 350 surface. After 1 week, initial large porous activated sludge flocs appeared due to the coagulation of bacteria sticking to CFH 350 but the size of these flocs were uneven. These flocs had swamp and loose structure and no obvious granulation was achieved (Fig. 7a).

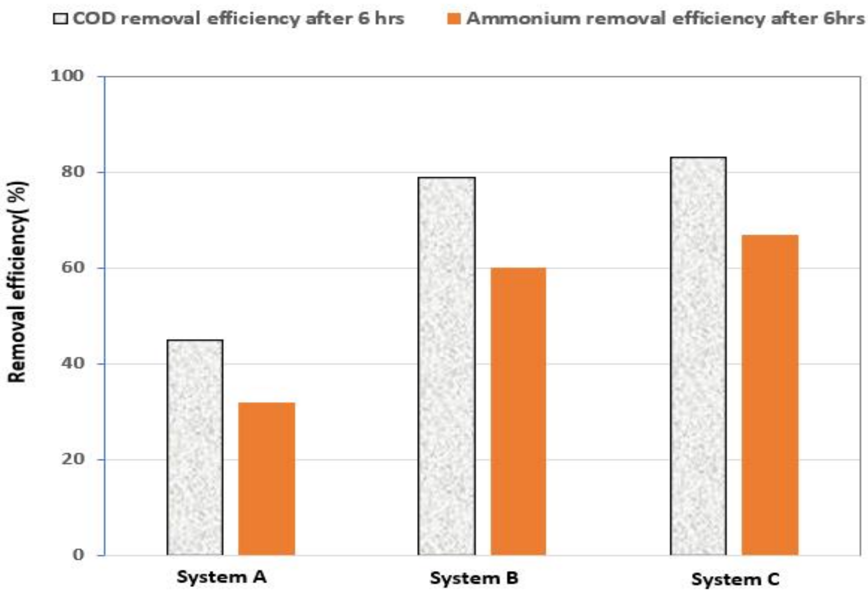

Figure 6. Removal efficiency of COD and ammonium in different system.

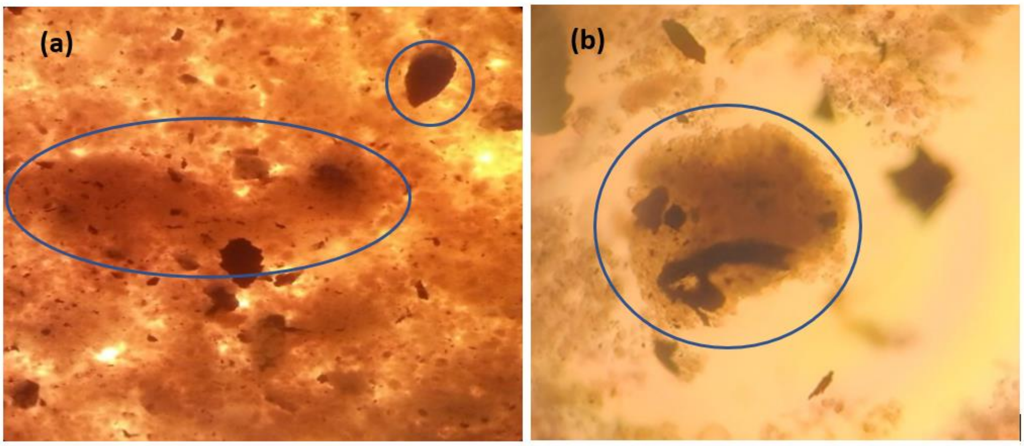

Figure 7. Biochar and activated sludge combination after 1 week (a) and after 3 weeks (b).

After 3 weeks of maintaining the operating mode of the SBR system, flocs completely covered the surface of the CFH 350 and a number of granular sludges were formed, a clear boundary between the granular layer and inner core was observed (Fig. 7b). The structure of granular sludge was tougher, but the surface of granule was still rough, not smooth and the granular size ranged from 1.0 - 2.0 mm. A recent research suggested that sludge granulation was significantly enhanced by addition of 0.2 mm activated carbon. However, there was no obvious improvement in granulation in reactor amended with 0.6 mm activated carbon. Hydraulic analysis revealed that increase- of granular activated carbon size enhanced the velocity field difference between flocs and activated carbon, which decreased the lifecycle and fraction of flocs-activated aggregates, suitable sizes (0.2 mm) could be served as the nucleating agent to accelerate flocs activated carbon coaggregation and formation of aerobic granules [25].

4. CONCLUSIONS

The obtained results showed that CFH 350 made from coffee husk pyrolyzed at low temperature, un-activated, did not only inhibit the development of activated sludge but also promoted the growth of activated sludge and increasing the adhesion of sludge onto biochar surface. The particles size of biochar and the ratio of biochar and activated sludge could be an important factor which affects the adsorption and adhesion capacity of activated sludge on biochar. The combination system of coffee husk biochar and activated sludge could remove COD and ammonium in wastewater when operating in batch experiment, nevertheless the treatment efficiency increased not significantly at the first stage of operating the system. COD and ammonium removal were mainly responsible by the microorganism in the activated sludge and biochar. The preliminary study could be considered as a potential research direction to evaluate the possibility of combining biochar with activated sludge towards forming granular sludge system.

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REFERENCES

1. Feng S., Xie S., Zhang X. - Ammonium removal pathways and microbial community in GAC-sand dual media filter in drinking water treatment, Journal of Environment Science 24 (9) (2012) 1587-1593.
2. Gupta V. K., Sadegh H. - Removal of ammonium ions from wastewater. A short review in development of efficient methods, Global Journal of Environment Science and Management **1** (2) (2015) 149-158.
3. Mazloomi F., Jalali M. - Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions, Journal of Environmental Chemical Engineering **4** (2016) 240-249.
4. Uğurlu M., Karaoğlu M.H.- Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: isotherm, kinetic and thermodynamic analysis, Microporous Mesoporous Mater. **139** (2011) 173-178.
5. Kizito S., Wu S., Kipkemoi K. W. - Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry, Science of the Total Environment **505** (2015) 102-112.
6. Wang H., Guo F., Shen G., Yang Y., Zhang Y. - Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium, nitrate and phosphate, Chemosphere **119** (2015) 646-653.
7. Meyer S., Glaser B., Quicker P. - Technical, economical, and climate-related aspects of biochar production technologies: a literature review, Environmental Science & Technology **45** (2011) 9473-9483.
8. Yao Y., Gao B., Zhang M., Inyang M., Zimmerman A.R. - Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil, Chemosphere **89** (2012) 1467-1471.
9. Tan X. F., Liu Y. G., Gu Y. L., Liu S. B., Zeng G. M., Cai X. - Biochar pyrolyzed from MgAl-layered double hydroxides pre-coated ramie biomass (Boehmeria nivea (L) Gaud.): Characterization and application for crystal violet removal, Journal of Environment Management **184** (2016b) 85-93.
10. Ahmed M. B., Zhou J. L., Ngo H. H., Guo W., Chen M. - Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater, Bioresource Technology **214** (2016) 836-851.
11. Kalyak Y., Mok-Ryun Y., Jae-Kyu Y., Yoon-Young C. - Adsorption of TNT and RDX Contaminants by Ambrosia trifida L. var trifida Derived Biochar, Research Journal of Chemistry and Environment **17** (4) (2013) 62-71.
12. Zheng W., Guo M. X., Chow T., Bennett D. N., Rajagopalan N. - Sorption Properties of Green waste Biochar for Two Triazine Pesticides, Journal of Hazardous Materials **181** (2010) 121-126.
13. Sarkhot D. V., Ghezzehei T. A., Berhe A. - Effectiveness of biochar for sorption of ammonium and phosphate from dairy effluent, Journal of Environment Quality **42** (5) (2013) 1545-1554.
14. Nguyen T. L., Nguyen P. D., Tran T. N. - Study on granulation of activated sludge using sequencing batch airlift reactor for COD and Ammonia removal, Science & Technology Development **12** (2) (2009) 39-50.

15. Gai X., Wang H., Liu J., Zhai L., Liu S. - Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate, PLoS ONE **9** (12) (2014). e113888.
16. Hao Z., Zhenyu W., Xia D., Jian Z., Ye L., Jeff N., Stephen H. - Characteristics and nutrient values of biochars produced from giant reed at different temperatures, Bioresource Technology **130** (2013) 463-471.
17. Sun D. Q., Meng J., Lian H., Yang E., Huang Y.W., Chen W. F., Jiang L. L., Lan Y., Zhang W. M., and Gao J. P. - Effect of volatile organic compounds absorbed to fresh biochar on survival of Bacillus mucilaginosus and structure of soil microbial communities, Journal of Soils and Sediment **15** (2) (2015) 271-281.
18. Yin Q., Liu M., Ren H. - Biochar produced from the co-pyrolysis of sewage sludge and walnut shell for ammonium and phosphate adsorption from water, Journal of Environment Management **249**(2019) 109410.
19. Liang P., Yu H., Huang J., Zhang Y., Cao H. - The Review on Adsorption and Removing Ammonia Nitrogen with Biochar on its mechanism, MATEC Web of Conferences 67:07006 (2016).
20. Yao T., Samrat A., Kurt O. K., Daniel S. A., Shengnan X., WeiJun T., Yang L. Y. - Influence of pyrolysis temperature on production of digested sludge biochar and its application for ammonium removal from municipal wastewater, Journal of Cleaner Production **209** (2019) 927-936.
21. Tao S., Wu Z., He X., Ye B., Li C. - Characterization of biochar prepared from Cotton stalks as efficient inoculum carriers for Bacillus subtilis SL-13, Bioresources **13** (1) (2018) 1773-1786.
22. Jia T., Lian Q., Xiaoying L., Bolin L., Junnan C., Juan Y., Yitian S., Xiaoguo C. - Effect of granular activated carbon on the aerobic granulation of sludge and its mechanism, Bioresource Technology **236** (2017) 60-67.
23. Li Z., Zhang X., Xiong X., Zhang B. W. - Determination of the best conditions for modified biochar immobilized petroleum hydrocarbon degradation microorganism by orthogonal test, IOP Conference Series: Earth and Environmental Science **94** (2017) 012191.
24. Li W., Carlos L., David E. C., Zulfiqar A. - Performance of a two-phase bio-trickling filter packed with biochar chips for treatment of wastewater containing high nitrogen and phosphorus concentrations, Process Safety and Environmental Protection **102** (2016) 150-158.
25. Jiaheng Z., Hang Z., Miao H., Hai-tian Y., Xiang-yang X., Julia V., Pedro J. J. A., Liang Z. - Granular activated carbon as nucleating agent for aerobic sludge granulation: Effect of GAC size on velocity field differences (GAC versus flocs) and aggregation behavior, Bioresource Technology **198** (2015) 358-363.