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Study on treatment of high ammonium concentration in piggery wastewater using rice husk biochar

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ABSTRACT : *The treatment of ammonia in water and wastewater has been receiving a lot of attention due to its harmful effects on the environment and water sources. There are many methods used to treat ammonium that have been extensively studied in recent years, including adsorption method. Materials that can adsorb ammonium in water and wastewater are numerous and varied, including natural materials and man-made materials. Currently, the tendency to use biodegradable materials as biological adsorbents are being emphasized. This study evaluates the ability of ammonium adsorption in wastewater using biochar made from rice husk. Initial research results showed that this material has good ammonium adsorption capacity, especially using modified biochar. The adsorption efficiency of biochar can be up to 92%, with an initial ammonia concentration of 200 mg/L and a solid/ liquid (S/L) ratio of 10 g/L, maximum adsorption capacity was 30 mg/g within contact time of 180 minutes. The research was applied on piggery wastewater after treatment using biogas tank with ammonium content of 150 mg/L also gave good results. The efficiency of ammonium treatment was 80% with a shaking time of 180 minutes, a solid / liquid ratio of 10 g/L. The advantage of using biochar was the ability to make use of cheap and easy-to-source materials. In addition, after adsorption, the adsorbed material can be used as a substrate for planting trees or fertilizers.*

KEYWORDS: *ammonium removal, biochar, bio-adsorption, piggery wastewater, rice husk*

I. INTRODUCTION

Ammonium pollution in water and wastewater has become one of the most serious problems nowadays as many types of wastewater contain high levels of Nitrogen(N) and Phosphorous(P) after treatment by conventional biotechnology which did not meet the discharge standard of effluent. Studies on treatment of ammonium in water and wastewater have been widely implemented and the recent trend is to use cheap biosorbents made from agricultural by-products as well as from industrial wastes [1,2,3,4]. The use of biochar or carbonaceous charcoal is one of the current promising research directions. In Viet Nam, recently, many types of biochars were made from agricultural wastes such as sawdust, rice husk, corncob, coffee skin ... have been applied in the treatment of nutrient-rich wastewater with high efficiency while reducing the cost of processing and materials [5,6,7]. After adsorption process, the biochar could be used as soil improvement fertilizer. Currently, in Vietnam, almost farms used biogas technology to treat wastewater. After passing through the biogas reactor, the organic matter in animal wastewater was reduced considerably however the ammonia content in wastewater was still very high, the BOD_5/TN ratio was low which made it difficult for the further biological treatment. Therefore, this study focused on ammonium treatment in biogas wastewater using biochar made from rice husk before and after activation.

II. MATERIALS AND METHODS

Preparation of biochar : Rice husk from agriculture wastes were collected, classified then cut from 1-5mm in size before pyrolysis at 450^oC in 30 minutes using continuous multi-zone rotation kiln. Samples of coal have an ash percentage of 20-22% and a fix carbon (FC) percentage of 42 - 43%. The SEM imagine showed the surface structure and porous structure of biochar made from rice husk (Fig. 1). Results of BET analysis measured the surface area of coal made from food waste was from 360-380 m^2/gr.

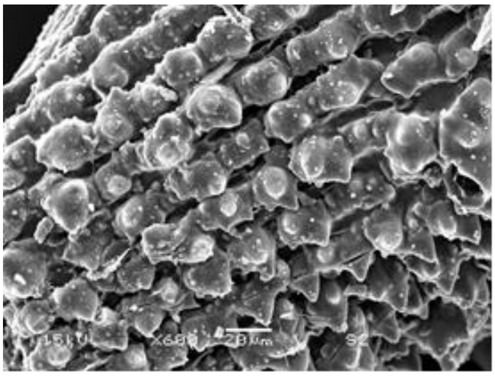


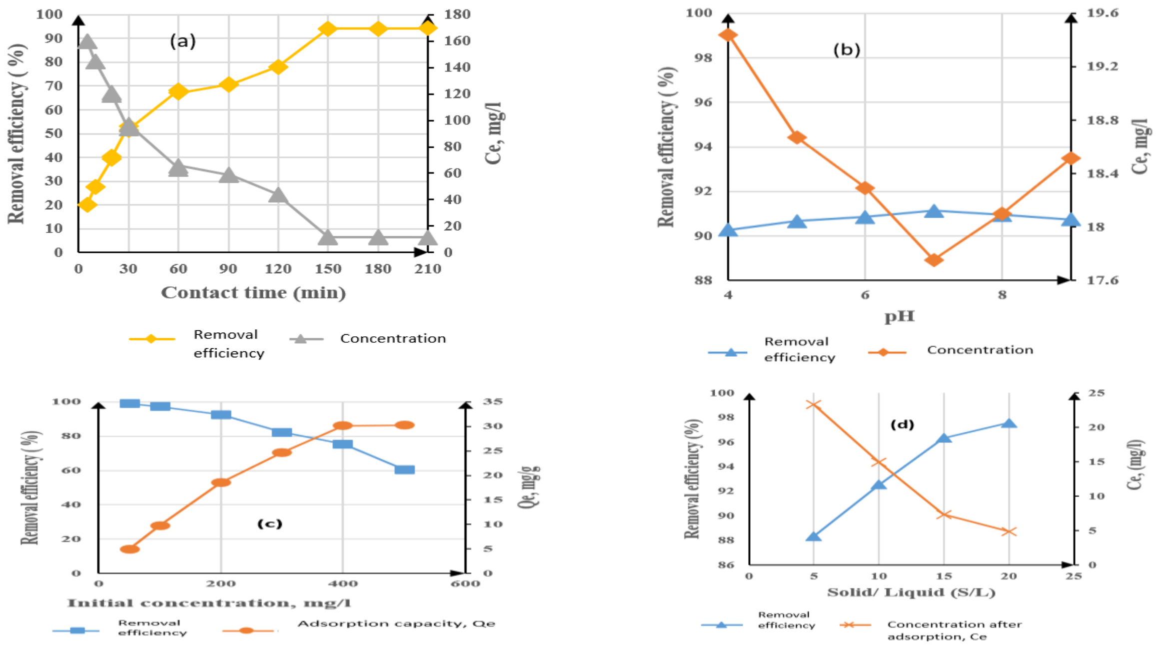
Fig 1. SEM images of rice husk biochar

Chemicals and apparatus : All chemicals are analytical grade from Merck. Ammonium stock solution was obtained by dissolving a quantity of NH_4Cl salt in deion water. The stock solution was diluted with deion water to produce working solution (as synthetic wastewater). HNO_3 and NaOH solutions were used for pH adjustment. Ammonium was analysed using Nitrogen Ammonia reagent set, TNT, Amver Salycylate, HACH; TN was analysed using Persulfate Digestion HR Method 10072, HACH; TP was analysed using Molybdovanadate with Acid Persulfate Digestion Method, HACH.

Batch adsorption studies: The experiments were conducted in batch mode in a 150mL triangular flask at 30^{o}C, agitated at constant speed of 200 rpm, to evaluate the adsorption capacity of ammonia in synthetic wastewater using biochar made from rice husk. The influence of some factors such as contact time, initial pH, initial ammonium concentration, solid/liquid(S/L) ratio, etc were determined. Later, the survey was conducted with wastewater from piggery farm after biogas process to assess the applicability of ammonia removal in wastewater using biochar before and after activation.

III. RESULTS AND DISCUSSION

Experiment with synthetic wastewater using unmodified biochar : Some factors affecting the efficiency of ammonium adsorption in synthetic wastewater by biochar were studied as effects of contact time, initial pH, the initial ammonium concentrations, the solid / liquid ratio (S / L), size of biochar and the shaking speed. The results were shown in Fig. 2 a, b, c, d,e,f



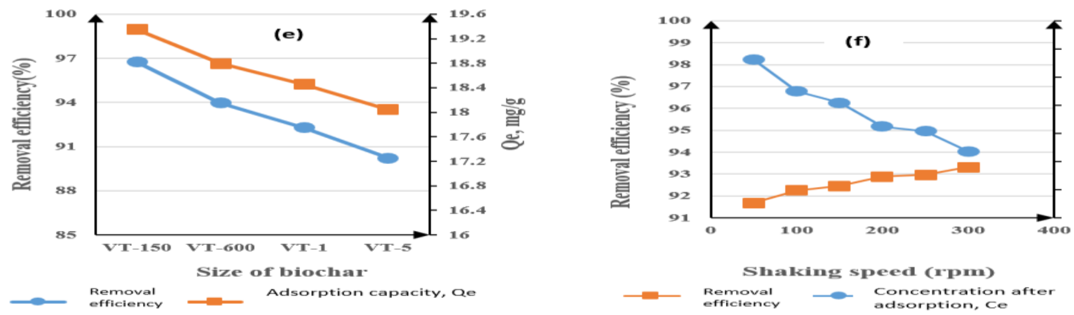


Fig 2. Effect of contact time (a), pH (b), solid/ liquid ratio(c), initial ammonium concentration (d) on ammonium adsorption, size of biochar (e) and shaking speed(f) on ammonium removal efficiency

The effect of contact time was investigated for a period of 210 minutes using an initial ammonium concentration of 200 mg/L at 30°C and pH=6.8, agitated at constant speed of 200 rpm, solid/liquid = 10g/L, particle size of material from 1-5mm. The results (Fig.2a) showed that the ammonium adsorption increased with time much more linearly from 30 to 150 min. After that, from 150 to 210 min the adsorption gradually becomes slower until equilibration. The trend could be explained in three ways; first the initial rapid uptake was a physical process occurring mainly through mass transfer based on ion concentration gradient between the solid and liquid phases. The second slower phase depicts the end of physical adsorption and corresponds to the ionic balance between the solid and liquid phase with slight desorption occurring for the physically bound ammonium ions. Finally, the much slower and more gradual increment corresponds to chemical adsorptions and some extent intrapartical diffusion which continues until saturation of the active sites. A similar trend had been reported in other studies [1, 2, 3].

Fig.2b showed the effect of initial solution pH on the adsorption of ammonium at Co = 200 mg/L; 180 mins, agitated at constant speed of 200 rpm, solid/liquid = 10 g/L. From the figure, as the pH increased from 4 to 8 the percentage removal increased and reached 92 %. At pH 9, the adsorption takes a decreasing trend. The decrease in adsorption at pH = 8 could be attributed to the fact that most of the ammonium was converted to NH_3 which cannot be adsorbed on to the adsorbent. Some previous ammonium adsorption studies have reported similar results [1, 2, 3].

To investigate the effect of solid/liquid ratio, some conditions were applied: initial ammonium concentration of 200 mg/L at 30°C and pH=6.8, agitated at constant speed of 200 rpm, pH =6.8, particle size of materials (150 µm; 600 µm, 1mm and 5 mm). The results (Fig. 2c) showed that when increasing the solid /liquid ratio from 5 to 15 gr / L, the adsorption efficiency increases rapidly (from 85% ÷ 95%) and slowly increased with the solid /liquid ratio of 20 g / L achieving 96% ÷ 97%. The result was similar when compared with other biochars made from other bio-materials with the same solid /liquid ratio [7,8,9].

The initial ammonium concentration varied from 50 ÷ 500 mg / l in order to evaluate the treatment efficiency of the material with different initial ammonium concentrations. The results (Fig.2d) indicated that as the concentration increased from 50 to 500 mg/L, the removal efficiency deceased but the amount adsorbed(mg/g) at equilibrium (Qe) increased significantly (from 5 mg/g ≅ 30 mg/g). The implication of this could be that as the concentration of ions increased there was correspondingly an increased mass flow of ammonium to the biochar active sites due to the build-up of anionic gradient between the solid and liquid phase and hence increased adsorbed amount. Similar results were obtained when compared to the maximum adsorbed capacity of other studies such as 20 mg/g with coconut fiber and 22,6 mg/g corncob biochar [5,6]. When the biochar size increased from 150µm to 5mm, the efficiency of the charcoal husk was reduced by 99% to 90%. This may be explained that the smaller the surface area of the material, the higher diffusion rates of adsorbents [8]. Smaller particles size would have shorter diffusion paths and they had a better chance of being adsorbed because the ions penetrated all of the pores inside the adsorbents. Both graphs showed that the adsorption capacities were proportional to the adsorption efficiency, but both efficiency and adsorption capacity were not much reduced by increasing the size of the material, generally removal efficiency reached more than 90% (Fig. 2e). The adsorption efficiency of the material increased when shaking speed increased, accelerating from 50-200 rpm, and slowing down from 200-300 rpm.

This could be deduced that as the increased in the movement of ammonium ions with the adsorbent increased the adsorption capacity and speed of 200 rpm was the maximum speed. Too fast movement reduced the adsorption capacity of the ammonium ion on the surface of the material. Compared to other materials available in [1,2] the shaking speed of 100 to 300 rpm with carbon-materials to zeolites gave the removal efficiency varies from 20% to 80%. As the speed of shaking was faster than 200 rpm, materials would be adhesion on the wall of the tank and could not exposed to the solution thus the adsorption efficiency reduced as a result (Fig.2f).

Similar to batch tests, kinetic experiments were done with ammonium concentration from 20- 500 mg/L; contact time from 5 -210 mins, shaking at constant speed of 200 rpm, solid/liquid = 10 g/L, particle size of material from 1-5mm, 30^{o}C and pH = 6.8.

Langmuir isotherms constants equation:

$$\frac{Ce}{q} = \frac{1}{qmax}.Ce + \frac{1}{qmax.KL}$$

Freundlich isotherms constants equation: $$\ln qe = \ln KF + \frac{1}{n}\ln Ce$$

From Table 1, on the basis of the observed R^2 values both the Langmuir model and Freundlich model fitted the data suggesting that ammonium adsorption both occurred by chemisorptions and physical-sorption. Similar biochar adsorption studies have reported ammonium adsorption to fit both the Langmuir and Freundlich models [8, 9].

Table 1. Model fit data for Langmuir and Freundlich isotherms constants

Langmuir coefficient		
q_{max} (mg/g)	K_L (l/mg)	R^2
22.92	4.03	0.99
Freundlich coefficient		
N	K_F (mg/l.g)	R^2
1.93	4.04	0.98

In order to understand the thermodynamic phenomena of ammonium adsorption onto the biochar, adsorption data using initial ammonium concentration of 200mg/L after 180 minutes equilibration time. It was noticed that the values of the correlation coefficients (R^2) for the pseudo-second order model are higher than those for pseudo-first-order model. However, comparing the calculated maximum adsorption values (q_1 and q_2) with the experimental values (q_e), the calculated values (q_1) for the pseudo-first-order model were in close range with the experimental values (q_e) whereas the calculated values from the pseudo-second-order model (q_2) higher than the experimental values thus the data fit to the pseudo-first order kinetic model (Table 2).

Table 2. Model fit data for the kinetic equations using synthetic wastewater

Pseudo first order coefficient			q_e, mg/g
$k_1 \times 10^3$, min^{-1}	q_1 , mg/g	R^2	
22.7	38.43	0.9051	38
Pseudo second order coefficient			
$k_2 \times 10^4$ g/mg.min	q_2,mg/g	R^2	
7.39	42.37	0.987	

Experiment with wastewater from piggery farm after biogas process : Characteristic of wastewater from piggery farm after anaerobic process (biogas): COD = 396 ÷ 893 mg/L; BOD_5 = 110÷150 mg/L; NH_4^+_N = 108

÷ 150 mg/L; TN = 465 ÷ 585 mg/L; PO_4^{3-} = 18 ÷ 56 mg/L; TP = 46 ÷ 64 mg/L; SS = 300 ÷ 402 mg/L; pH = 6.4 ÷ 7.2.

When conducting adsorption in 180 minutes, the solid/liquid ratio of 10 g/L, the efficiency of ammonium treatment in wastewater after biogas with the above characteristics was only 53%, much smaller than the results obtained with the synthetic wastewater (91%). This could be explained that the synthetic wastewater contained only ammonium however livestock wastewater contained many other components (COD, TN, TP, PO_4^{3-}, NO_3^-, heavy metals…) and suspended solid which could clog the adsorbed material, sealing of porous holes on the material, reducing the surface area of the material thus reduced the ability of adsorption of ammonium ion. In order to increase the capacity of ammonium treatment, biochar samples were modified to increase the surface area, the size of the porous holes inside the material as well as function groups on the surface thereby increasing the adsorption capacity of the biochar [10,11,12].

Biochar samples of two different sizes of 600µm (named as VT_1) and 2-5mm (VT_2) were activated with 3N HCl (VT_1-HCl, VT_2–HCl); NaOH 3N (VT_1-NaOH, VT_2–NaOH); and distilled water (VT_1-H_2O, VT_2-H_2O) at 50°C for 24 hours at a ratio of 10gr of activated charcoal per 200 mL of activated solution. After activation, the biochar samples were filtered and washed with distilled water and adjusted the pH of the solution after washing to neutral (pH 7). Later, these biochars were dried in a freezer and put into desiccant equipment. The results of research on ammonium adsorption efficiency in wastewater from piggery farm after anaerobic digestion was shown in Fig 3. Biochar with small particle size (600µm) also gave the lower ammonium removal efficiency than biochar with the large particle size (1-5mm). It was due to the fact that piggery wastewater contained high smooth SS content which could enter the pores inside the material, reducing the surface area of the material and reducing the material's efficiency especially the materials with small particle size. When removing the effect of SS in the effluent, the adsorption efficiency increased by 5% when the wastewater was settled, increased by about 15% after filtration and after centrifugation the efficiency increases by 20%, reached up to 80%. It was seen that the suspended solid content in wastewater affected the adsorption efficiency of biochar.

Moreover, the study also investigated the effect of some elements in piggery wastewater such as Suspended solid (SS), COD, Total Nitrogen (TN) and Total Phosphorous (TP) on the overall treatment efficiency of biochar. To assess the effect of suspended solids, the experiment was conducted with the effluent after sedimentation, after filtration and after centrifugation. Besides, assessing the ability of ammonium removal in wastewater, the study also evaluated preliminary the removal efficiency of some other parameters such as COD, TN, TP. The results were shown in Fig 4. In addition to the removal percentage of ammonium with nearly 80%, there were also other factors in wastewater were removed such as COD ≅ 20%, TN ≅ 30% and TP ≅ 70%.

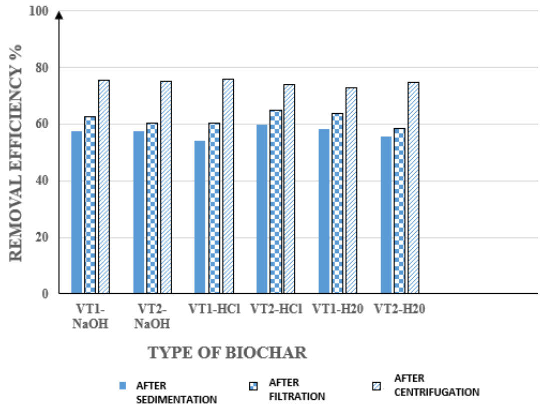


Fig.3. Effect of SS on ammonium removal efficiency

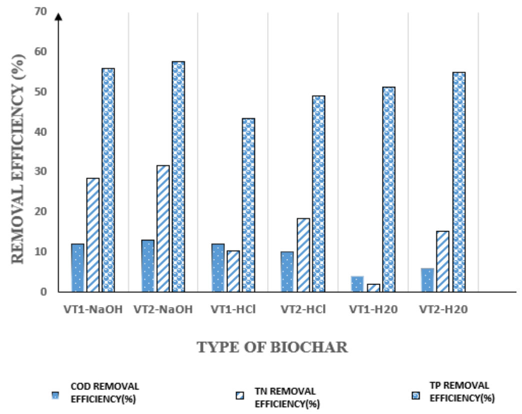


Fig.4. Removal efficiency of COD, TN and TP

IV. CONCLUSION

Initial research results showed that biochar made from agriculture waste (rice husk) before and after activation had the ability to adsorb ammonium in wastewater from piggery farm after biogas process relatively well. Adsorption efficiency was 53% when using inactivated biochar and increased up to 80% when using activation biochar. Besides, the effective treatment of ammonia in piggery farm wastewater after biogas, biochar produced from rice husk was capable of adsorbing other substances in piggery wastewater such as COD (20%); TN (40%) and TP (70%) with an adsorption time of 3 hours. These results also indicated the prospect of practical use of low-cost biochar for further treatment of ammonium and other organic pollutants in wastewater.

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