The Isotherm Studies Of Adsorbent Development From Pulogadung Primary Sewage Sludge (PS) With Rice Straw Addition By Hydrothermal

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Abstract. The rapidly amount of primary sludge (PS) by pass production from wastewater treatment plant becomes problematic worldwide due to the release of some toxic substances from PS if directly dispose to the landfill. Hydrothermal treatment (HTT) has been reported to be able to immobilize heavy metals and generated bio-char, and silicate-based minerals for the potential development of adsorbent. This study investigated the feasibility of adsorbent development from HTT sludge and also addition of rice straw then tested the performance of the developed adsorbent for ammonia removal from synthetic ammonia wastewater. Rice straw (RS) addition can enhance ammonia adsorption capacity of all the developed adsorbents (HTT150+RS; HTT175+RS; HTT200+RS). The maximum ammonia adsorption capacity for developed adsorbents (HTT150+RS; HTT175+RS; HTT200+RS) were approximately 37-40 mg-N/g-SS, about 70-80 % of ammonia adsorption capacity of zeolite used in this work. The Hydrothermal of PS + RS indicates is a potential bio-sorbent.

Keywords — Sewage Sludge; Rice straw; Hydrothermal; Adsorbent

1. Introduction

Most of the treatment units in wastewater treatment plants consist of part screening, sedimentation, grit chamber, and biological reactors produce sludge, one of the major by-products from wastewater treatment. Treatment and disposal of sludge are dependent on its volume and characteristics. The general classification of wastewater sludge is based on their production source (Figure 1), such as primary sludge (PS) from the primary sedimentation tank, secondary sludge from the secondary sedimentation tank, waste activated sludge from the waste sludge stream, anaerobic digested sludge from anaerobic digestion tank, etc.

![Figure 1. General treatment processes in wastewater treatment plants (Source: Nirotech, Indonesia, 2015)](image-url)
Recently, the increasing production of sludge or sewage sludge becomes problematic worldwide, including in Indonesia. The high contents of organic, moisture, and complexity of nitrogen with other composition including a large amount of ionic pollutants and toxic substances are containing in sewage sludge. Due to its massive quantity and characteristics, disposal management of sewage sludge finds some difficulties. The amount of nitrogen (N) is about 1% up to 18% being in organic form (Johannesson, 1999). If nitrogen substances can be stabilized, it is useful to improve the productivity of soil (Barzegar et al., 2002). Recently, finding some applicable, cost effective and safe treatment method for sewage sludge becomes a popular and urgent challenge since sewage sludge would become a serious environmental problem if disposed or discharged directly into a landfill or aquatic life ecosystems. In the past, the simplest disposal method for sludge is landfilling, but it is not sustainable for a long period because of causing sanitary problems and groundwater contamination. Hydrothermal treatment (HTT) is one of the promising thermal methods to treat sewage sludge. HTT is one of the combination processes involving dehydration and decarboxylation of biomass. Hydrothermal technology is usually operated under the following conditions (Funke and Ziegler, 2010; Ito et al., 2015). Shi (2014) reported that HTT was able to immobilize heavy metals and reduce toxicants in the treated sludge. Bio-char and silicate-based minerals were generated during HTT. 80% of the water content release under HTT and the bypass product can be use as an alternative fertilizer or fuel (Mitsubishi Nagasaki Machinery Mfg.Co.Ltd., 2012). On the other hand, HTT was reported to be able to convert organics (peanut hull and rice husk) to a potential adsorbent material (Liu and Zhang, 2009; Michael, 2014). Peanut hull and rice husk can be converted to adsorbent by HTT and utilized to adsorb ammonium nitrogen from wastewater (Saleh et al., 2013). Initially, Rice straw (RS) and PS were mixed then treated by HTT to enhance NH\textsubscript{4}\textsuperscript{+} removal capacity of developed adsorbents. The purpose is to investigate and study the isotherm model of developing adsorbent from PS by adding RS addition with HTT on ammonia adsorption capacity of the PS-derived adsorbents. Batch experiments were also used to investigate the effect of initial ammonium concentration, and equilibrium isotherms on the developed adsorbents. Synthetic zeolite was also used as an adsorbent control in this study.

### 1.1 Kinetics study

Mathematic models are necessary for information extraction and process optimization, which can provide insight into performance capacity of the system. Isotherm study is applied to characterize the adsorption equilibrium, capacity (Wen et al., 2006; Huang et al., 2010) and mechanisms (Zheng et al., 2008). The exchange of NH\textsubscript{4}\textsuperscript{+} can be studied by using different types of equilibrium isotherm models such as Freundlich, Langmuir, Brunauer-Emmett-Teller, Henry, Redlich-Peterson, Dubinin-Radushkevich, Temkin (Hameed et al., 2008). Among them, Freundlich and Langmuir isotherm models are the most commonly used models for analyzing equilibrium data (Zheng et al., 2008). Freundlich isotherm is applied to multilayer adsorption with non-uniform distribution over the heterogeneous surface. It gives a logarithmic relationship between the solid and liquid concentrations. It is helpful in correlating isotherm data collected over a wide range of concentration. The Freundlich equation can be expressed as in equation 1 (Hameed et al., 2008):

\[
q_e = K_F C_e^{\frac{1}{n}}
\]

where, \(q_e\) is the amount of NH\textsubscript{4}\textsuperscript{+} adsorbed per unit weight of adsorbent (mg/g). \(C_e\) is the equilibrium concentration of NH\textsubscript{4}\textsuperscript{+} remaining in solution (mg/l). \(K_F\) represents Freundlich isotherm constant (mg/g) and \(1/n\), heterogeneity factor, represents adsorption capacity of adsorbent and a constant relating to adsorption intensity or surface heterogeneity.

Freundlich equation can be linearized by logarithmic as equation 2 (Hameed et al., 2008; Zheng et al., 2008):

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]
Langmuir isotherm assumes monolayer adsorption with the uniform distribution of energetic adsorption sites. It can be written as equation 3 (Zheng et al., 2008):

\[
\ln q_e = \ln K_L + \frac{1}{n} \ln C_e
\]

where, \( q_e \) is the equilibrium amount of NH\(_4^+\) exchanged by adsorbent (mg/g). \( q_{\text{max}} \) is the maximum uptake of ammonia, \( C_e \) is the equilibrium concentration of NH\(_4^+\) remaining in solution (mg/l) and \( K_L \) is the Langmuir constant (l/mg) which is determined by the intercept and the slope of the linear plot. Langmuir equation can be rearranged into the linear form as equation 4 (Zheng et al., 2008; Huang et al., 2010):

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]

### 2. METHODOLOGY

PS was sampled from a wastewater treatment (IPAL Pulogadung) Jakarta. During the experiments, PS was kept and stored in a refrigerator at 5 °C. RS collected from a paddy field area in Bekasi, Indonesia was used as additional material to enhance the ammonia removal of the developed adsorbent. The physicochemical characteristic of RS used in the experiments is shown in table 1 (Shi, 2014). Synthetic zeolite in the experiments was from Wako Pure Chemical Industries, Ltd. The type of synthetic zeolite is Zeolite A-4 (Na\(_2\)O·Al\(_2\)O\(_3\)·2SiO\(_2\)) with particle size of 0.4 – 0.5 mm. Zeolite A-4 was used as a control and standard or reference without purification in the batch adsorption experiments.

**Table 1.** Physicochemical characteristics of rice straw used in this study

| Items                   | Rice straw     |
|-------------------------|----------------|
| Total solid (TS) %      | 90.1 ± 0.3     |
| Volatile solid (VS) %   | 79.4 ± 1.1     |
| Lignin (g/100g-DM)      | 14.6 ± 1.9     |
| Cellulose (g/100g-DM)   | 28.2 ± 0.3     |
| Hemicellulose (g/100g-DM)| 17.5 ± 3.1   |

(Shi, 2014)

#### 2.1 Hydrothermal pretreatment of PS

HTT was performed by using the batch reactor shown in figure 2. Five mg RS was added and mixed with 100 ml PS during HTT at the designated peak temperature (150, 175 or 250 °C). And the subsequent procedures such as solid/liquid separation and calcinations were shown in figure 3. No calcination scenario was also conducted to prepare the PS-derived adsorbent for comparison. All the developed adsorbents were collected and used for batch adsorption experiments.
2.2 Batch adsorption experiments

Ammonia removal performance of PS-derived adsorbent was evaluated by conducting batch adsorption experiments. These experiments were conducted at temperature 25 °C by using the shaker (MMS-310, Tokyo Rikakikai Co., Ltd.). Ammonium chloride was used to prepare the synthetic wastewater (ammonium chloride solution), which was purchased from Wako Pure Chemical Industries, Ltd. Ammonium chloride solution was prepared by using certain ml of distilled water to make the different initial concentration of ammonium nitrogen.

2.3 Isotherm models

The Freundlich and Langmuir models were used to analyze the results from batch ammonium experiments and characterize the exchange equilibrium of ammonium nitrogen uptake by adsorbents when initial ammonium nitrogen concentration varied from 1000 to 7000 mg-N/l.

2.4 Other analytical and calculation methods

Other parameters like total solids (TS) and volatile solids (VS) were measured according to standard methods (APHA, 1999). Total nitrogen (TN) and ammonia-N concentrations in liquid were quantified with persulfate method and phenate method (APHA, 1999; Park et al., 2009), respectively.
3. Results and discussion

3.1 Nitrogen release during HTT after RS addition

Based on the Figure 4, ammonia-N and total N concentrations in the liquid phase were detected to increase after adding rice straw under the different HTT temperature (HTT150+RS; HTT175+RS and HTT200+RS). The existing forms of nitrogen in the liquid after rice straw addition are mainly ammonia-N and organic-N, and the increment in TN is most probably contributed by RS addition and enhanced hydrolysis of PS in HTT.

![Figure 4. Effect of RS addition on nitrogen release during HTT](image)

3.2 Changes in adsorption performance of PS-derived adsorbents after rice straw addition

Figure 5 shows the ammonia adsorption onto all tested adsorbents increased after adding RS (initial ammonia-N concentration in synthetic wastewater was 1800 mg/l). The equilibrium ammonia adsorption amount of the PS-derived adsorbents after RS addition (HTT150+RS; HTT175+RS; HTT200+RS) was almost similar with zeolite, about 10.4, 11.7, and 12.0 respectively within 30 min in comparison to 13.0 mg/g-SS for zeolite. This observation might be brought about by increased contents of silica or aluminosilicate minerals in the resultant adsorbents after RS addition (Saleh et al., 2013; Huang et al., 2015). Since carbon and silica are main components, RS has the potential to be used as a raw material or additives in composite adsorbent for ammonia removal. In addition, during the thermal treatment (HTT) the surface site of RS might be open up. Figure 6 also shows similar ammonia adsorption capacity was achieved at different initial ammonia-N concentrations after rice straw addition into PS during HTT and calcination processes.
3.3 Isotherm study

(1) Freundlich isotherm model

The Freundlich equilibrium isotherm model was used in this study to fit the experimental data for NH$_4^+$ adsorption on the tested adsorbents (HTT150+RS; HTT175+RS; HTT200+RS) as shown in figure 7. The values of $K_F$ and $n$ were again determined by calculating the intercept and slope of the plot (Table 2). $K_F$ values for the developed adsorbents (HTT150+RS; HTT175+RS; HTT200+RS) are 0.88, 1.04 and 0.90, respectively. All plots had similar $R^2$ ranging between 0.950 - 0.980. The dimensionless constant $n > 1$ for all of the tested adsorbents, meaning that these adsorbents (HTT150+RS; HTT175+RS; HTT200+RS) were suitable to remove NH$_4^+$.
Figure 7. Linear plots of Freundlich isotherm for PS-derived adsorbents after RS addition
(a) HTT150+RS; (b) HTT175+RS; (c) HTT200+RS; (d) RS
Table 2. Coefficients determined for PS-derived adsorbents after RS addition by using Freundlich isotherm

| Adsorbent  | $K_F$ | n   | $R^2$ |
|------------|-------|-----|-------|
| HTT150+RS  | 0.88  | 1.52| 0.950 |
| HTT175+RS  | 1.04  | 1.50| 0.957 |
| HTT200+RS  | 0.90  | 1.53| 0.978 |
| Zeolite     | 2.34  | 1.35| 0.993 |
| RS         | 0.76  | 1.51| 0.979 |

(2) Langmuir isotherm model

Langmuir isotherm model was plotted by a linear equation of $C_e$ against $C_e/q_e$ as shown in figure 8, and the values of $K_L$ and $q_m$ were derived from the intercept and slope of the plot, respectively. Compared to Freundlich isotherm, Langmuir model shows a slightly lower fitness to the data of PS-derived adsorbents with the addition of RS (HTT150+RS; HTT175+RS and HTT200+RS). Based on the Table 3, the $q_m$ values for both developed adsorbents increased after RS addition ranging between 37 – 40 mg-N/l. It was indicated the addition of RS improved the maximum capacity of developed adsorbents from PS. It was obvious that HTT200+RS had higher affinity to ammonia and better adsorption performance on ammonia removal.

Table 3. Coefficients determined for PS-derived adsorbents after RS addition by using Langmuir isotherm

| Adsorbent  | $K_L$ | $q_m$ | $R^2$ |
|------------|-------|-------|-------|
| HTT150+RS  | 1,347 | 37.45 | 0.906 |
| HTT175+RS  | 1,140 | 37.88 | 0.906 |
| HTT200+RS  | 1,106 | 39.37 | 0.959 |
| Zeolite     | 85.60 | 55.55 | 0.995 |
| RS         | 0.76  | 30.67 | 0.957 |
4. Conclusions & Recommendations

4.1 Conclusions

PS with RS addition (100 ml-PS/5 mg-RS) was conducted. HTT and calcination processes were performed to improve bio-sorbent capacity at HTT temperatures (150 °C, 175 °C, 200 °C). The results showed that the developed adsorbents with RS addition (HTT150+RS, HTT175+RS, and HTT200+RS) exhibited similar behavior with the control at all initial ammonia-N concentrations. Within 30 minutes, the ammonia adsorption amount of developed adsorbent (HTT150+RS, HTT175+RS, and HTT200+RS) and zeolite were 10.4, 11.7, 12.0 and 13.0 mg/g-SS, respectively, when the initial ammonia-N concentration was 1800 mg/l. Then the isotherm adsorption investigation showed that developed adsorbents with RS addition were suitable to remove NH₄⁺ and HTT200+RS had a higher affinity to ammonia.
4.2 Recommendations

In order to obtain more comprehensive results, the further experiments like investigating the adsorption kinetics and mechanisms and also finding another potential additional materials in order to enhance the maximum adsorption capacity.

5. References

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