Nitrate removal from aqueous solution by adsorption using municipal solid waste-derived activated biochar

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Abstract. Nitrate is considered as a major groundwater pollutant causing serious health and environmental effects. In this study, the removal of nitrate from aqueous solutions using municipal solid waste-derived activated biochar (MSWAB) via adsorption was explored. Initially, municipal solid waste (MSW), another prominent source of environmental pollution, was used as feedstock to produce biochar, which was chemically activated using potassium hydroxide, producing MSWAB. Activation of MSWAB resulted to an increase in surface area from 2.5 to 6.5 m²/g. The effect of initial nitrate concentration (A), pH (B), and adsorbent dosage (C) on nitrate removal were then evaluated using a 2k factorial experimental design. Results show that initial nitrate concentration, pH, and two-way interactions AB and AC have significant effects on % nitrate removal. Nitrate removal was found to increase as the initial nitrate concentration and pH decreases. Using Response Surface Methodology (RSM), the local optimum conditions for maximum nitrate removal of 66.97% were determined to be at 30 mg/L initial nitrate concentration and pH 2 at 10 mg/mL adsorbent dosage. The appropriate isotherm for nitrate adsorption onto MSWAB was the Freundlich isotherm. Comparison with commercial activated carbon (CAC) in terms of nitrate removal efficiency at local optimum conditions showed that MSWAB is inferior to CAC. However, it is still notable that MSWAB was able to reduce the nitrate concentration from 30 mg/L to 11.27 mg/L which satisfies the 14 mg/L DENR effluent standard for Class C water bodies, showing its potential as an alternative adsorbent for treatment of nitrate-laden wastewaters.

1. Introduction

Nitrate (NO₃⁻) is an ion formed by the oxidation of nitrogen and is considered as one of the world’s major groundwater pollutants along with nitrite (NO₂⁻). For developing countries like the Philippines, groundwater remains an important water resource especially in areas out of public services’ reach[1]. According to Powlson and Addiscott[2], nitrate is the main form of nitrogen which plants consume. High occurrence of nitrate contamination is found in areas where nitrogen fertilizers are commonly used[3]. In the Philippines, nitrogen-based fertilizers like urea and ammonium sulfate are the most commonly used and imported fertilizers[4]. Statistics provided by the Food and Agriculture Organization[5] for 2016 show that fertilizer consumption in the country for nitrogen alone reached 617,069.76 tonnes. Despite the assurance of higher nutrient uptake in plants, excessive use of fertilizers can lead to accumulation of nitrogen and other nutrients in water bodies through leaching and surface runoff[2]. Aside from nitrogen-based fertilizers, nitrate contamination can also come from animal manure and sewage or septic waste[6]. The phenomenon of nutrient accumulation, known as eutrophication, can lead to decreased oxygen levels and biodiversity in bodies of water due to increased algal blooms and can also cause health problems in humans[7][8].
Solid waste management is another prominent problem in the Philippines. According to the Department of Environment and Natural Resources\[9\], waste generated in the country is expected to increase up to 16 million metric tons by 2020 and one of the primary contributors are the different types of municipal solid wastes (MSW), which pertain to all non-hazardous solid or semi-solid waste from residential, commercial, and industrial sources. The Republic Act 9003 or the Ecological Solid Waste Management Act of 2000 aims to properly address waste generation problems in the country by mandating local government units to establish waste management programs in their respective areas\[10\]. However, other factors, such as financial limitations, compromise the effectiveness of implementation in some areas of the country. Thus, there is a need to look into alternative methods to decrease waste generation aside from the existing waste management types in the country, which are sanitary land filling and the 3 R’s (Reduce, Reuse, Recycle)\[11\].

According to Oonk and Boom as cited by Jayawardhana et al.\[12\], the increasing amount of solid waste and its corresponding amount of emission when degraded can be simultaneously addressed by converting municipal solid waste into biochar. It is a carbon-rich product of pyrolysis which can be utilized both in the production of energy and of adsorbents according to Bernardo et al. as cited by Jin et al.\[13\].

Adsorption is a process in which components of liquids or gases adhere to surfaces of solids, which are referred to as adsorbents\[14\][15]. Various studies have been conducted to test the applicability of biochar as an adsorbent, usually in adsorption processes for the removal of heavy metals, nutrients, and organic substances present in wastewaters. The use of biochar is cheaper and requires lower temperatures in production compared to activated carbon, which is the most commonly used adsorbent\[16\].

In relation to nutrient contamination, a study by Hina\[17\] has shown that activated pine biochar has the potential to remove nitrogen and phosphorus present in wastewater via adsorption. On the other hand, Manyuchi, et al.\[18\] found that biochar from organic waste can be used for nutrients recovery from municipal wastewater, specifically total Kjeldahl nitrogen and phosphorus. The concentration of another form of nitrogen, ammonium (\(\text{NH}_4^+\)), was also found to significantly decrease after adsorption using biochar derived from rice straw\[19\]. Biochar modified using Mg and Al have also shown excellent co-adsorption of nutrients such as nitrate, ammonium, and phosphate\[20\]. However, adsorption is not the method commonly used in the treatment of nitrogen, specifically nitrate, in wastewaters. More commonly used methods are ion exchange, reverse osmosis, and electrodialysis which have higher energy requirements, implying higher capital costs compared to adsorption\[21\].

Thus, this study tested the potential of MSW-derived activated biochar (MSWAB) as an alternative to commercial activated carbon in nitrate removal. Optimum conditions, specifically initial nitrate concentration, pH, and adsorbent dosage, for the removal of nitrate using the adsorption process were also determined.

2. Methods

2.1. Production of MSW-derived biochar

MSW was collected from residential, institutional, and commercial areas located within Los Baños, Laguna. The waste collected included kitchen/food waste, plastics, paper, glass, and other organic and inorganic waste.

The method of production of MSW biochar was patterned to that of Requiero\[19\] and Genuino et al.\[20\]. The different components of MSW collected were sun-dried then subjected to oven-drying at 60ºC for 48 hours. After drying, the MSW was size reduced using the multi-purpose shredder and hammer mill. The crushed MSW was then sieved using standard mesh -16+30, mixed, and stored in an airtight container.

For pyrolysis, fabricated AISI 316 stainless steel reactors, each containing 50 grams of sieved MSW, were used. Nitrogen was then purged into the reactors for two minutes, then the reactors were placed in
a VULCAN® A-550 furnace. The temperature was allowed to reach 500°C and was held for 30 minutes. The reactors were then cooled down to room temperature and the MSW biochar (MSWB) were collected, weighed, and stored in an airtight container.

2.2. Activation and Characterization of MSW-Derived Biochar

The method for chemical activation of MSW-derived biochar employed by Jin et al. [13] was used, with minor modifications. A ratio of twenty-five grams of MSWB to 100 mL of 2 M KOH solution was used. Constant stirring at 500 rpm for 60 minutes was employed. The biochar was then filtered and washed with dilute HCl and distilled water until neutral pH. The precipitate was then dried using a hot plate at 105°C for 8 hours. After recovery, the activated biochar (MSWAB) was weighed and stored in an airtight container.

The MSWB and MSWAB were characterized using Micromeritics Gemini VII 2390 Surface Area Analyzer at 77 K to determine the surface area. Micrographs of the biochar samples were also obtained using Zeiss Ultra Plus Field Emission-Scanning Electron Microscope (FE-SEM).

2.3. Standard Curve Determination for Calibration Constant

For the determination of standard curve for each adsorption experiment, the method from the American Public Health Association [21] was followed. Eight 50 mL solutions having 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 mg NO₃-N/L concentrations were prepared by dilution of the 100 mg NO₃-N/L stock solution. For each solution, 1 mL of 1 M HCl was added to prevent interference of other ions with the nitrate ions [22]. The corresponding absorbance of the eight solutions was read using UV 1280 UV-VIS Spectrophotometer at wavelengths of 220 nm and of 275 nm in order to determine the absorbance due to nitrate.

\[
Abs_{NO_3^-} = Abs_{220nm} - (2 \times Abs_{275nm})
\] (1)

The calibration constant was then determined using the Beer-Lambert’s Law (Equation 2). The absorbance due to nitrate values were plotted against the corresponding concentrations of each NO₃-N solutions

\[
A = abc
\]

where:

\( A \) is the absorbance

\( a \) is the molar absorptivity

\( b \) is the path length

\( c \) is the concentration

2.4. Determination of Equilibrium Time for Adsorption

According to Tabing as cited by Bondoc [23], the equilibrium time is the point at which the sample concentration reaches a constant value. Contact periods ranging from 10 minutes to 8 hours were used. For each contact period, 50 mL of 60 mg /L NO₃-N was mixed with two MSWAB dosages, 1.25 mg/mL and 10 mg /mL, in a 125-mL Erlenmeyer flask and placed on a shaker. After every contact period, 1 mL of 1 M HCl was added after diluting 1 mL of each nitrate solution to 25 mL. Their respective absorbances were then determined via UV-VIS spectrophotometer to determine their concentrations using a standard curve. The time at which the concentration became constant served as the equilibrium time and was used as the contact time for the succeeding adsorption experiments.

2.5. Parametric Analysis for Nitrate Removal via Adsorption onto MSWAB

In the determination of the effect of the factors, initial nitrate concentration, pH, and adsorbent dosage, a 2s factorial design with four center points generated using Design Expert 11 was used.

Low and high levels of 50 mg NO₃-N/L and 250 mg NO₃-N/L were used to test the effect of initial nitrate concentration. To test the effect of pH, low and high levels of 2 and 10, respectively, were used. The adjustment of the initial pH of the nitrate solution was done using 1 M HCl and 1 M NaOH. To test the effect of adsorbent dosage, low and high levels of 10 mg/mL and 50 mg/mL, respectively, were
used. Each run in the experimental design was done in a 125-mL Erlenmeyer flask subjected to constant shaking for the determined contact time.

Same with the standard solutions, 1 mL of 1 M HCl was added to each run after dilution to 25 mL to prevent interference of other ions[22]. The final absorbance of the NO$_3$–N solutions were read at 220 nm and at 275 nm to determine their respective concentrations. To quantify the effects, the percentage nitrate removal (Equation 3) was then calculated for each run. Analysis of Variance (ANOVA) at 95% confidence interval was used to test the significance of the factors used.

$$\% \, NO_3^{–} \, N \, \text{Removal} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100$$  \hspace{1cm} (3)

where:

- $C_0$ is the initial NO$_3$–N concentration
- $C_f$ is the final NO$_3$–N concentration

2.6. Optimization of Adsorption Process

After the parametric analysis, the optimum conditions for NO$_3$–N removal was determined. Response Surface Methodology (RSM) using Central Composite Design (CCD) was used. A full RSM was performed since the levels of the initial nitrate concentration were adjusted to 30 mg/L and 100 mg/L, for the low and high levels, respectively. The levels of the other factors in the parametric analysis were retained.

After performing the full RSM experiment, the specific goals for optimization which were to maximize nitrate removal, to minimize adsorbent dosage, and to have both initial nitrate concentration and pH in range were set. The solution with the highest desirability generated by Design Expert 11 was chosen. For validation, five samples were prepared with the initial nitrate concentration, pH, and MSWAB dosage adjusted to that of the generated solution. The % nitrate removal of the five samples were determined and the mean was then compared to that of the predicted value.

2.7. Determination of Adsorption Isotherm

In determining the best fit isotherm, five (5) NO$_3$–N solution concentrations, 20, 40, 60, 80, and 100 mg/mL, were used. The optimum pH and adsorbent dosage determined in the optimization experiment were used. The adsorption capacity and the equilibrium concentration were obtained to determine the best fit isotherm. The adsorption capacity can be calculated using Equation 4[22].

$$q_e = \frac{V(C_0 - C_e)}{w}$$  \hspace{1cm} (4)

where:

- $q_e$ is the equilibrium adsorption capacity
- $V$ is the volume of the solution
- $w$ is the dry mass of the adsorbent used
- $C_0$ is the initial NO$_3$–N concentration
- $C_e$ is the equilibrium NO$_3$–N concentration

The values of $q_e$ and $C_e$ were substituted to the linearized Freundlich (Equation 5) and Langmuir (Equation 6) isotherms. The constants for each isotherm were determined by linear regression.

$$\log q_e = \log K_f + \left( \frac{1}{n_f} \right) \log C_e$$  \hspace{1cm} (5)

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m} \right) C_e + \frac{1}{q_m K_L}$$  \hspace{1cm} (6)

2.8. Comparison of Performance with Commercial Activated Carbon

The performance of MSWAB in NO$_3$–N adsorption was compared to that of commercial activated carbon produced by MAPECON Green Charcoal Philippines, Inc. The adsorption conditions were adjusted to that of the optimum conditions determined and the same contact time were used. The residual concentration was determined also by absorbance readings at 220 and 275 nm and the
percentage NO₃–N removal of commercial activated carbon was then calculated using Equation 3 and served as the basis for comparison.

3. Results and Discussion

3.1. Yield and Characteristics of Municipal Solid Waste-Derived Activated Biochar

The production of MSW resulted in an overall average yield of about 49.79% in terms of weight of MSWAB produced per weight of raw MSW used. The pyrolysis temperature, heating rate, and losses after collection from filtration, washing, and drying are factors which affected the yield of MSWAB. According to Basu [24], lower temperatures and heating rates result in higher amounts of biochar produced. This is because at higher temperatures, the dehydration and elimination reactions for the production of volatile matter occurs at a higher rate, leading to higher gas yields and lower biochar yields[25][26].

Raw MSW and MSWAB were also characterized in terms of surface area to determine if it is suitable for adsorption. The BET surface area of biochar was found to increase from 2.6 m²/g (MSWB) to 6.5 m²/g (MSWAB) after KOH treatment. According to Fu et al.[27], pore structure development in biochar occurs when volatile matter is lost during pyrolysis which causes the increase in total pore volume and surface area. The increase in surface area can also be attributed to a proposed mechanism for KOH activation of biochar, which is the reaction between the potassium species and carbon from the biochar surface which results to etching[20]. The surface areas obtained, however, are low even after activation. Mopoung et al. [28] also obtained a low surface area (2.72 m²/g) from KOH for activation of tamarind seeds biochar, which was attributed to the accumulation of potassium compounds from the activating agent on the surface. Additional washing can be done in order to remove the residual activating agent[29].

The micrographs obtained using FE-SEM illustrating the porous structure of MSWB and MSWAB produced in this study are shown in Figure 1. The structure observed in Figure 1(a) indicates that even before activation, the MSWB produced is already porous, which is desirable for adsorbents. Adhered particles were observed on the surface of MSWAB in Figure 1(b), which are possibly residues from the activating agent, KOH, which were not completely washed off.

3.2. Equilibrium time for nitrate adsorption

Equilibrium time is defined as the time at which the concentration of the nitrate solution starts to become constant during adsorption process. The equilibrium time also reflects the maximum adsorption capacity under the set conditions since the adsorption capacity remains nearly constant as well after reaching the equilibrium time[30]. Thus, the equilibrium time was determined in order to ensure that the potential of MSWAB as adsorbent would be properly evaluated in the latter adsorption experiments.

The equilibrium time was determined by monitoring the residual nitrate concentration after set contact periods. Residual nitrate concentrations were measured after constant shaking. Nitrate concentration was observed to decrease for the first 20 minutes then fluctuated until the end of the test at 480 minutes.

Although the residual concentration was observed to approach a constant value at 20 minutes, the equilibrium time chosen was 120 minutes. First, this is to ensure that the adsorbent has equilibrated well with the solution since in the latter adsorption experiments, varying initial nitrate concentrations...
were used. Second, the percentage difference of the residual concentration was considered. The residual concentrations of the solutions at 90 and at 120 minutes only had 0.72 % and 0.48 % difference, for the low and high adsorbent dosages, respectively, which indicates that the residual concentration is almost constant at 120 minutes. Several nitrate adsorption studies also reported that equilibrium was attained after 60-90 minutes[31][32]. Lastly, adsorption using commercial activated carbon (CAC) for nitrate removal, which was also done in this study, was also considered. According to Öztürk and Bektas[33], the equilibrium time for nitrate adsorption using powdered activated carbon was 45 minutes. Hence, at 120 minutes contact time, it can be ensured that both MSWAB and CAC would reach their maximum adsorption capacities.

### 3.3. Factors affecting nitrate adsorption

The effects included in the discussion are only those found to be significant using ANOVA at 95% confidence interval (effects with p-values less than 0.05). These include the main effects of initial nitrate concentration and pH (both with p-values < 0.0001), the interaction effect of initial nitrate concentration and pH (p-value < 0.0001), and the interaction effect of initial nitrate concentration and adsorbent dosage (p-value = 0.0179).

#### 3.3.1. Effect of initial nitrate concentration

The % nitrate removal increases as the initial nitrate concentration decreases. According to Bekele et al.[22], this is because at higher concentrations, the diffusion rate onto the adsorbent is higher which causes the adsorbent to be saturated easily. Once the MSWAB reaches saturation or its maximum adsorptive capacity, the concentration of the residual nitrate solution will start to remain constant. Since more nitrate ions are present at higher initial concentrations, there will be higher competition for available adsorption sites.

#### 3.3.2. Effect of pH

The % nitrate removal was found to decrease as the pH increases. This can be explained by the excess amounts of OH- ions present in the solution. The excess OH- ions surround the surface of the adsorbent which results to electrostatic repulsion with the nitrate ions (NO₃⁻) since both are negatively charged[31]. On the other hand, at acidic conditions, the surface is surrounded by H+ ions which favors the adsorption of nitrate driven by electrostatic attraction[31]. Other studies also reported that the surface properties of the adsorbent vary with pH which can also affect the adsorption of nitrate. In a study by Iida et al.[34] where the surface of activated carbon was modified by introducing basic groups like pyridine using ammonia gas treatment, the removal of nitrate was promoted at lower pH since more protons accumulated at the basic surface. In the case of MSWAB, a basic surface is possible since it was activated using a strong base, KOH. This explains the higher nitrate removal at acidic conditions due to accumulation of H+ on the basic surface.

#### 3.3.3. Effect of initial nitrate concentration and pH interaction

The results of the ANOVA also showed that the interaction effect of the initial nitrate concentration and pH has a significant effect on the % nitrate removal. The effect of pH on % nitrate removal is more evident at low initial nitrate concentrations. At low initial nitrate concentration, the % nitrate removal decreases as the pH increases. Aside from the lower amounts of nitrate ions present, acidic conditions tend to favor the adsorption of nitrate as discussed earlier, which led to lower residual nitrate concentrations, and consequently, higher % nitrate removal. On the other hand, at high initial nitrate concentration, there is no significant change in % nitrate removal as the pH increases. Even at the expected favorable acidic conditions, the adsorption of nitrate was relatively low. This shows that the initial nitrate concentration affects the adsorption efficiency more than the pH, since at high initial nitrate concentration, the effect of pH becomes insignificant. It is possible that at high initial nitrate concentration, the adsorbent was easily saturated, which is why there was no significant difference on % nitrate removal observed at varying pH levels.

#### 3.3.4. Effect of initial nitrate concentration and adsorbent dosage interaction

Adsorbent dosage, as a main effect and within the range 10 to 50 mg MSWAB/mL NO₃⁻ solution, was found to have no significant effect on the % nitrate removal. However, its interaction with the initial nitrate concentration
was found to be significant. There is an increase in the % nitrate removal as the adsorbent dosage was increased at low initial nitrate concentrations. On the other hand, at high initial nitrate concentrations, a slight decrease in % nitrate removal was observed when the adsorbent dosage was increased.

Generally, the % removal increases with the adsorbent dosage due to the presence of more active sites[35], which was the case at low initial nitrate concentrations. More adsorption sites as the dosage was increased accommodated more nitrate ions, leading to an increase in % nitrate removal. However, % removal may also be reduced due to lower effective surface area caused by overlapping adsorption sites[36]. Also, since the surface area of MSWAB is relatively low and heterogeneous, the available adsorption sites for the low and high dosages may not be significantly different.

As discussed earlier, high initial nitrate concentration can also cause the adsorbent to be saturated easily, leading to low % removal. The high initial nitrate concentration (250 mg/L NO3-N) might have also been too high for the capacities of the range of MSWAB dosage considered, causing the minimal difference in % nitrate removal.

3.4. Optimum conditions for nitrate adsorption onto MSWAB.

Optimization using Response Surface Methodology (RSM) was performed in order to determine the conditions that will give the highest % nitrate removal. The factors which were found to be significant in the parametric study were included in the optimization. The results of the parametric study also served as basis for possible adjustments in the levels of each factor which can result to the optimum conditions.

Adjustments were done only on the levels of the initial nitrate concentration. The levels were adjusted from 50 mg/L NO3-N and 250 mg/L NO3-N to 30 mg/L NO3-N and 100 mg/L NO3-N, respectively. The levels of the pH (2 and 10) and of the MSWAB dosage (10 mg/mL and 50 mg/mL) from the parametric study were retained since based on the model generated in the parametric study, the initial nitrate concentration is the factor with the largest effect on % nitrate removal.

It must be noted that the optimum conditions identified in this study are the local optimum conditions, meaning the values obtained are all within the range of levels used. Capturing the global optimum conditions requires re-adjustment of the levels of the factors in order to attain higher % nitrate removal. However, based on the adjusted levels used in RSM, it is not reasonable to adjust these levels further due to cost requirements for pH adjustment and the limitation of using simulated solutions only. It is possible that the optimum conditions that will be determined will not necessarily result to the expected % nitrate removal when applied to actual wastewater since other factors, like the presence of other ions, might affect the adsorption process. However, identifying at least the local optimum conditions will help narrow down the range of conditions that favors nitrate adsorption to be covered in further studies.

The solution which was selected from the generated solutions for optimization by Design Expert 11 predicted 70.56 % optimum removal and the conditions were at 30 mg/L initial nitrate concentration, pH 2, and 10 mg/mL MSWAB dosage. After performing the adsorption process at the selected conditions using 5 replicates, the validity of the prediction was checked. Since the value of the data mean, 66.97 %, is in between the values of the 95 % confidence interval and had only 5.22 % difference with the predicted mean, the prediction of the model can be considered valid. In addition, the average residual nitrate concentration of the confirmatory runs is 11.27 mg/L, which satisfies the 14 mg/L NO3-N DENR effluent standard for Class C water bodies.

3.5. Adsorption isotherm for nitrate adsorption onto MSWAB

Isotherms represent the capacity of an adsorbent and its functional dependence on the amount of adsorbate present[37]. To identify the appropriate adsorption isotherm, the adsorption capacity at equilibrium, qe, was determined at varying initial nitrate concentrations. The qe and equilibrium concentrations were then fitted to the Langmuir and Freundlich isotherms which commonly describe water and wastewater treatment applications[37].

The Langmuir isotherm assumes that only a monolayer adsorption occurs at specific sites which are homogeneous and have equal adsorption energies[32][38]. The other parameters that can be obtained from the linearized form are the maximum monolayer adsorption capacity, qm, and the Langmuir constant, KL. A higher value of KL indicates higher adsorption energy, or in this case, the tendency of the nitrate to be adsorbed onto the MSWAB’s surface or active sites[38].
On the other hand, the Freundlich isotherm applies to multilayer adsorption and it assumes that the surface of the adsorbent and the site energies are heterogeneous\[38\]. The intercept, $K_f$, provides a rough indication of the adsorption capacity while the slope, $1/n$, provides adsorption intensity\[37\]. A value between 0 and 1 for the slope is desired since it indicates a favorable adsorption isotherm. A value closer to zero indicates higher surface heterogeneity and non-linear adsorption, while values greater than 1 indicate unfavorable adsorption\[38\]. The parameters for both adsorption isotherms are summarized in Table 1.

| ISOTHERM   | $R^2$ | PARAMETER | VALUE |
|------------|-------|-----------|-------|
| Langmuir   | 0.9950| $q_m$ (mg/g) | 2.1127|
|            |       | $K_L$     | 0.4035|
| Freundlich | 0.7376| $1/n$     | 0.1901|
|            |       | $K_f$     | 0.9646|

Comparing the values of $R^2$ for the Langmuir and Freundlich isotherms, the Langmuir isotherm indicates a better fit for the adsorption process. However, it must be noted that one of the assumptions of the Langmuir isotherm is that the surface of the adsorbent is homogeneous. Based on the results of the parametric and optimization studies, the insignificance of the MSWAB dosage on the % nitrate removal was attributed to the heterogeneity of the surface, which does not satisfy the assumption of the Langmuir isotherm. In an examination of the Langmuir isotherm in a study by Harter as cited by Foo, et al.\[39\], considering an insufficient range of adsorbate concentration (in this case, nitrate ions) can lower the variability of model’s linearity. This is a possible explanation for the high values of $R^2$ obtained for the Langmuir isotherm despite its assumptions not being satisfied since the concentration range considered is only 20-100 mg NO₃-N/mL.

Although the Freundlich isotherm had a lower $R^2$, it can describe the nitrate adsorption process better. It is also supported by the value of $1/n$ approaching 0, which indicates heterogeneous surface of the adsorbent. As discussed earlier, it is possible that the presence of functional groups on the surface of MSWAB may not be uniform throughout the mixture due to components which do not contain carbon and are non-combustible. Thus, it is possible that the adsorption energies at these sites also differ, in case chemical adsorption is also present. This makes Freundlich isotherm the more appropriate isotherm to describe the nitrate adsorption process onto MSWAB.

### 3.6. Comparison of MSWAB with commercial activated carbon.

After the determination of the optimum conditions, the performance of MSWAB was compared to commercial activated carbon (CAC). The same amount of dosage (10 mg/mL), initial nitrate concentration (30 mg/L NO₃-N) and pH (pH 2) as local optimum conditions were used. Even though literature values for the equilibrium time of powdered activated carbon for nitrate adsorption was considered in setting the equilibrium time to maximize capacity, it must be noted that the comparison of the performance of MSWAB and CAC is still limited to the local optimum conditions generated for MSWAB.

The difference between the % nitrate removal of the two adsorbents was found to be significant after performing t-test. CAC gave higher average nitrate removal of 79.11 % as compared to MSWAB which gave an average removal of 66.97 %. This can be explained by the superiority of the surface area of CAC over that of MSWAB, which is usually 500 m²/g or more\[40\]. Also, in a study by Öztürk and Bektas\[33\], high nitrate removal was observed for activated carbon at pH 2, which may have favored the adsorption better. Still, there is potential for MSWAB for nitrate adsorption since at local optimum conditions, it was able to achieve an average of 11.27 mg NO₃-N/L concentrations that satisfy the DENR effluent standard for Class C water bodies. Also, the use of MSWAB can be considered since the main problem with CAC is its high cost.

### 4. Summary and Conclusions
In this study, nitrate removal from aqueous solution using activated biochar via adsorption was explored. Municipal solid waste was used as feedstock for pyrolysis to produce biochar which was subsequently activated using potassium hydroxide.

An overall yield of 49.79 % weight MSWAB per weight raw MSW was obtained, while the surface area of the pristine biochar increased from 2.6 m²/g to 6.5 m²/g after activation using KOH.

For nitrate adsorption using MSWAB, the effects of initial nitrate concentration, pH, and adsorbent dosage on nitrate removal efficiency were initially determined using a 2³ factorial experiment. The determination of optimum adsorption conditions was subsequently conducted following Response Surface Methodology. The results of the parametric study show that the initial nitrate concentration, pH, the two-way interaction of initial nitrate concentration and pH, and the two-way interaction of initial nitrate concentration and adsorbent dosage significantly affect % nitrate removal from aqueous solution via adsorption. Increasing initial nitrate concentration decreases the % nitrate removal. Moreover, high initial nitrate concentration causes the pH and adsorbent dosage to have negligible effects, which was attributed to the saturation of the nitrate ions in the solution. Decreasing the pH, on the other hand, increases % nitrate removal since nitrate adsorption is favored at acidic conditions due to electrostatic attraction.

The local optimum conditions for nitrate adsorption from aqueous solution using MSWAB were found to be at 30 mg/mL initial nitrate concentration, pH 2, and 10 mg/mL MSWAB dosage, which resulted to 66.97 % nitrate removal. At 30 mg/mL initial nitrate concentration, adsorption at optimum conditions resulted to an average residual nitrate concentration of 11.27 mg/L, which conforms to the 14 mg/L effluent standards for Class C water bodies.

The behavior of the adsorption process is best described by the Freundlich isotherm since this isotherm assumes a multilayer adsorption and heterogeneous surface, which is the case for MSWAB. The parameters of the Freundlich isotherm also indicate a favorable adsorption.

Nitrate removal efficiency of MSWAB was also compared with that of commercial activated carbon at local optimum conditions for MSWAB. Although CAC has a higher removal efficiency, the MSWAB was still able to significantly reduce nitrate concentrations down to acceptable levels. Since the cost of activated carbon is high, MSWAB can be considered as a potential substitute.

Although inferior to the commercially available adsorbents, MSWAB shows potential in reducing nitrate concentrations in aqueous solutions. Aside from the treatment of nitrate-contaminated water, the use of MSWAB in nitrate adsorption can also aid in addressing high amounts of solid wastes.

5. References

[1] Umezawa Y, Hosono T, Onodera S, Siringan F, Buapeng S, Delinom R, Yoshimizu C, Tayasu I, Nagata T and Taniguchi, M 2008 Sources of nitrate and ammonium contamination in groundwater under developing Asian megacities Science of the Total Environment 407(9), 3219–3231. doi: 10.1016/j.scitotenv.2009.01.04

[2] Powlson DS and Addiscott TM 2005 Nitrogen in soils | Nitrates. Encyclopedia of Soils in the Environment 21–31. doi: 10.1016/B0-12-348530-4/00905-X

[3] Tirado R 2007 Nitrates in drinking water in the Philippines and Thailand. Greenpeace Research Laboratories Technical Note 10/2007. Retrieved September 15, 2018 from https://www.researchgate.net/publication/253389305_Nitrates_in_drinking_water_in_the_Philippines_and_Thailand

[4] Briones RM 2014 The Role of Mineral Fertilizers in Transforming Philippine Agriculture Philippine Institute for Development Studies Discussion Paper Series No. 2014-14. Retrieved September 15, 2018 from

[5] Food and Agriculture Organization of the United Nations Statistics Division 2016 Fertilizers by nutrient. Retrieved September 1, 2018 from http://www.fao.org/faostat/en/#data

[6] Beta Analytic Testing Laboratory 2018 Nitrate contamination and sources of nitrate pollution. Retrieved September 11, 2018 from https://www.betalabservices.com/nitrate-test/

[7] Rathore SS, Chandravanshi P, Chandravanshi A and Jaiswa K 2016 Eutrophication: Impacts of Excess Nutrient Inputs on Aquatic Ecosystem. IOSR Journal of Agriculture and Veterinary Science, 09(10), 89–96. doi: 10.9790/2380-0910018996
[8] World Health Organization. 2011 Nitrate and nitrite in drinking-water. Background Document for Development of WHO Guidelines for Drinking-Water Quality, 37(4), 227–231. doi: 10.1159/000225441

[9] Department of Environment And Natural Resources 2015 National solid waste management report (2008-2014). Retrieved September 1, 2018 from https://nswmc.emb.gov.ph/wp-content/uploads/2016/06/Solid-WasteFinalDraft-12.29.15.pdf

[10] Acosta V, Paul J, Lao C, Aguinaldo E and Valdez MDC 2012 Development of the Philippines National Solid Waste Management Strategy 2012-2016. *Procedia Environmental Sciences*, 16, 9–16. doi: 10.1016/j.proenv.2012.10.003

[11] Castillo AL and Otama S 2013 Status of solid waste management in the Philippines. Paper presented at the 24th Annual Conference of Japan Society of Material Cycles and Waste Management. doi: 10.14912/jsmcwm.24.0_677

[12] Jayawardhana Y, Kumarathilaka P, Herath I, and Vithanage M 2016 Municipal Solid Waste Biochar for Prevention of Pollution From Landfill Leachate. *Environmental Materials and Waste: Resource Recovery and Pollution Prevention*. Elsevier Inc. doi: 10.1016/B978-0-12-803837-6.00006-8

[13] Jin H, Capareda S, Chang Z, Gao J, Xu Y and Zhang J 2014 Biochar pyrolytically produced from municipal solid wastes for aqueous As(V) removal: Adsorption property and its improvement with KOH activation. *Bioresource Technology*, 169, 622–629. doi: 10.1016/j.biortech.2014.06.103

[14] Geankoplis JC 1993 Transport processes and unit operations (3rd ed.). New Jersey: Prentice-Hall.

[15] Seader JD and Henley EJ 2006 Separation process principles (2nd ed.). USA: John Wiley & Sons.

[16] Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y, and Yang Z 2015 Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*, 125, 70–85. doi: 10.1016/j.chemosphere.2014.12.058

[17] Hina K 2013 Application of biochar technologies to wastewater treatment. Unpublished doctoral dissertation – Soil Science. Massey University, Palmerston North, New Zealand.

[18] Golie WM, Ahmad K, and Upadhyayula S 2017 A Review on the Removal of Nitrate from Water by Adsorption on Organic-Inorganic Hybrid Biocomposites. *Advanced Materials for Wastewater Treatment*, 433–477. doi: https://doi.org/10.1002/978111911907805.ch12

[19] Requiero MCJ 2017 Parametric study on pyrolysis conditions for the yield and physico-chemical characteristics of biochar using waste cacao pod husk. Unpublished undergraduate thesis - Chemical Engineering. University of the Philippines Los Baños, College, Laguna.

[20] Genuin DAD, De Luna MDG and Capareda SC 2018 Improving the surface properties of municipal solid waste-derived pyrolysis biochar by chemical and thermal activation: Optimization of process parameters and environmental application. *Waste Management*, 72, 255–264. doi: 10.1016/j.wasman.2017.11.038

[21] American Public Health Association 1998 Standard methods for the examination of water and wastewater (20th ed.). Washington, DC: American Public Health Association.

[22] Bekele W, Faye G and Fernandez N 2014 Removal of nitrate ion from aqueous solution by modified ethiopian bentonite clay. *International Journal of Research in Pharmacy and Chemistry*, 4(1), 192–201. Retrieved September 29, 2018 from https://pdfs.semanticscholar.org/2e83/62266a64c394b9c10eaddf8a27f0e6a7e964.pdf

[23] Bondoc OJM 2018 Chromium removal from chrome-tannery effluent after alkaline precipitation by adsorption using durian shell-derived activated carbon. Unpublished undergraduate thesis - Chemical Engineering. University of the Philippines Los Baños, College, Laguna.

[24] Basu P 2010 Pyrolysis and Torrefaction. Biomass Gasification and Pyrolysis (First Edit). Elsevier Inc. doi: 10.1016/B978-0-12-374988-8.00003-9

[25] AlOthman ZA, Habila MA, and Ali R 2011 Preparation of Activated Carbon Using the Copyrolysis of Agricultural and Municipal Solid Wastes at a Low Carbonization Temperature, 24, 67–72. Retrieved April 25, 2019 from https://pdfs.semanticscholar.org/2f50/babf5eabebe96177506a9c38082b55ac3f.pdf
[26] Gopu C, Gao L, Volpe M, Fiori L and Goldfarb JL 2018 Valorizing municipal solid waste: Waste to energy and activated carbons for water treatment via pyrolysis. Journal of Analytical and Applied Pyrolysis, 133(April), 48–58. doi: 10.1016/j.jaap.2018.05.002

[27] Fu P, Hu S, Xiang J, Sun L, Yang T, Zhang A, Wang Y and Chen G 2009 Effects of Pyrolysis Temperature on Characteristics of Porosity in Biomass Char, 109–112. doi: 10.1109/ICEET.2009.33

[28] Mopoung S, Moonsri P, Palas W, and Khumpai S 2015 Characterization and Properties of Activated Carbon Prepared from Tamarind Seeds by KOH Activation for Fe (III) Adsorption from Aqueous Solution, 2015. doi: 10.1155/2015/415961

[29] Hagemann N, Id KS, Schmidt H, Böhler MA and Bucheli TD 1974 Activated Carbon , Biochar and Charcoal: Linkages and Synergies across Pyrogenic Carbon’s ABC’s, 1–19. doi: 10.3390/w10020182

[30] Nuradibah H, Chin SY and Anwaruddin H 2014 Study of Important Operating Parameters for the Adsorption of Acrylic Acid from Wastewaster Using Palm Ash. Journal of Applied Sciences, 14. 1385–1390. doi: 10.3923/jas.2014.1385.1390

[31] Bhutnagar A, Kumar E and Sillanpää M 2010 Nitrate removal from water by nano-alumina: Characterization and sorption studies. Chemical Engineering Journal, 163(3), 317–323. doi: 10.1016/j.cej.2010.08.008

[32] Cho D, Chon C, Kim Y, Jeon B, Schwartz FW, Lee E and Song H 2011 Adsorption of nitrate and Cr (VI) by cationic polymer-modified granular activated carbon. Chemical Engineering Journal, 175, 298–305. doi: 10.1016/j.cej.2011.09.108

[33] Öztürk N and Bektas TE 2004 Nitrate removal from aqueous solution by adsorption onto various materials, 112, 155–162. doi: 10.1016/j.jhazmat.2004.05.001

[34] Iida T, Amano Y, Machida M and Imazeki, F 2013 Effect of Surface Property of Activated Carbon on Adsorption of Nitrate Ion. Chemical and Pharmaceutical Bulletin, 61(11), 1173–1177. doi: 10.1248/cpb.c13-00422

[35] Kalantary RR, Dehghanifard E, Mohseni-Bandpi A, Rezaei L, Esrafili A, Kakavandi B and Azari A 2015 Nitrate adsorption by synthetic activated carbon magnetic nanoparticles: kinetics, isotherms and thermodynamic studies. Desalination and Water Treatment, 57:35, 16445–16455. doi: 10.1080/19443994.2015.1079251

[36] Onguyo MS, Masukume M, Ochieng A and Otieno F 2010 Functionalised natural zeolite and its potential for treating drinking water containing excess amount of nitrate, 36(5), 655–662. Retrieved April 27, 2019 from https://www.ajol.info/index.php/wsa/article/viewFile/61999/50049

[37] Weber WJ 1974 Adsorption processes. Pure and Applied Chemistry, 37(3), 375–392. doi: 10.1351/pac197437030375

[38] Saadi R, Saadi Z, Fazaeei R, and Fard NE 2015 Monolayer and multilayer adsorption isotherm models for sorption from aqueous media Monolayer and multilayer adsorption isotherm models for sorption, (May). doi: 10.1007/s11814-015-0053-7

[39] Foo KY and Hameed BH 2010 Insights into the modeling of adsorption isotherm systems, 156, 2–10. https://doi.org/10.1016/j.cej.2009.09.013

[40] Haycarb 2019 Activated carbon basics. Retrieved May 3, 2019 from https://www.haycarb.com/activated-carbon